STUDIES IN AROMATIC REACTIVITY

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STUDIES IN AROMATIC REACTIVITY

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ABSTRACT

The half-wave potentials of six series of Schiff bases, each of nineteen compounds, of the types ArCH=NAr' and ArN=CHAr', where Ar represents an unsubstituted aryl group and Ar' represents a phenyl group substituted in the meta or para positions, have been measured in dimethylformamide, using a mercury pool reference electrode. The effects on the half-wave potentials of changing the substituent in Ar' and of varying the structure of Ar have been investigated. Substituent effects have been examined in terms of the Hammett σ-ρ relationship and also in terms of a substituent constant, σ_{SB}, generated from the data of the Schiff bases (Series B) having the general formula $C_6H_5CH=NC_6H_4X$. Structural variations in Ar have been studied by adopting Series B as the standard Schiff base series and by generating substituent constants for each structure.

The values of the reaction constant, ρ, obtained in the present study range from 10.06 to 23.23 and are much larger than ρ values usually obtained in solution. These values are similar in magnitude to ρ values obtained in gas phase reactions. This suggests, in the polarographic reduction of Schiff bases in dimethylformamide, that solvent effects are virtually absent.

Variations in the half-wave potentials with structure of Ar for the unsubstituted aldehyde fragment of the molecules have been correlated with quantities derived from the perturbed molecular orbital version of the Huckel molecular orbital theory. Correlations between series of

Schiff bases of the type ArCH=NAr' (Ar=C_6H_5, 2-naphthyl, 9-phenanthryl, 9-anthryl) and a' correlation between two series of the type ArN=CHAr' (Ar=C_6H_5, 2-naphthyl) have also been obtained as predicted previously.

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CHAPTER 1

INTRODUCTION

During the 1920's and 1930's considerable interest was displayed in the possibility of deriving relationships between reaction rates and equilibria. While there were no theoretical reasons to account for the observations, relationships between rate and equilibrium constants were observed in some groups of closely related reactions. Brönsted proposed the first quantitative relationship of this kind, between the rates of certain acid-base catalysed reactions and the ionisation constants of the acids concerned.[1] This was written:

$$\log k = x \log K + \log G \qquad [1]$$

where k is the rate constant for the reaction, K the ionisation constant of the acid and x and G are constants.

The best known and most widely used linear free energy relationship is that proposed by Hammett in 1937.[2] This relationship quantitatively relates the effect of substituents in positions meta or para to a side chain in a benzene ring, to a rate or equilibrium constant of a reaction occurring in the side chain. This is normally expressed in the form:

$$\log K = \log K^{\circ} + \sigma\rho \qquad [2]$$

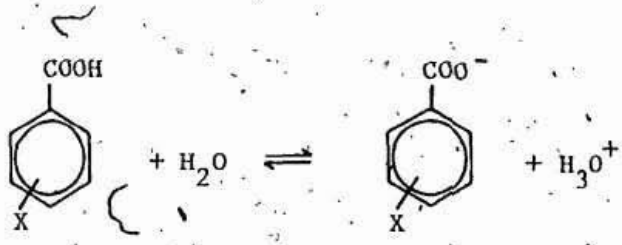
where K and K° are rate or equilibrium constants for the substituted and unsubstituted reactants respectively, σ is the substituent constant

and ρ the reaction constant.

1.1 The Substituent Constant

The general failure of Hammett's equation in the case of reactions at positions in the benzene ring, for substituents in the ortho position and for examples in which direct conjugation occurs between the substituent and reaction centre indicates that the variable correlated includes neither steric effects nor direct resonance effects, but that it is a function of the polar effects of substituents on the reacting group. This may reflect both inductive (electrostatic) and resonance (electronic) interactions of the substituent with the carbon atom of the benzene ring which carries the side chain reaction centre.

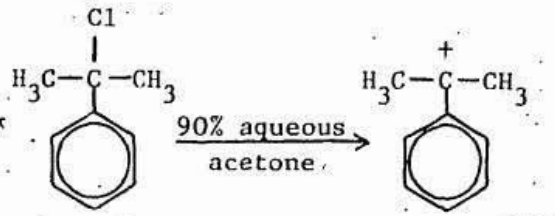
Hammett defined the substituent constants in terms of the relative acidities of the benzoic acids. For the reaction:



[3]

Hammett assigned an arbitrary value of unity to ρ. Consequently, the substituent constant, σ, was defined as $\log K - \log K^\circ$, where K° was the equilibrium constant for the unsubstituted acid (X = H) and K that of the acid substituted in the meta or para position. Electron withdrawing substituents strengthen the acids and these substituents have positive σ values; conversely, electron-repelling substituents have negative σ values. Substituent constants can

therefore be considered as a measure of the ability of groups to supply electrons to or withdraw electrons from the benzene ring. The values determined by Hammett were found to be unsatisfactory in reactions where powerful and direct conjugative interactions occurred between the substituent and the reaction centre. Enhanced σ values were found to be necessary for the strongly electron-attracting p-NO_2 and p-CN substituents in the ionisation of anilines and phenols; other similar electron-attracting para substituents which require enhanced σ values when they are in direct resonance with electron-rich reaction centres are listed by Jaffé.[3] These enhanced substituent constant values are denoted by σ^-. At the other extreme, strongly electron-repelling substituents, which are in direct resonance with electron-deficient reaction centres, or reaction centres at which a positive charge is generated, also gave divergent σ values. Okamoto and Brown[4] suggested a redefined σ in these cases, designated σ^+, based on the solvolysis of cumyl chlorides in 90% aqueous acetone at 25°C.



[4]

Both σ^+ and σ^- values successfully correlate reactions in which a substituent directly conjugates with the reaction site in either the reactant or product, but not in both.[5] Meta substituents cannot be involved in direct conjugation with the reaction site and therefore the meta substituent constant values do not differ significantly in

the three scales; however, differences in the values of σ (para), σ^+ (para) and σ^- (para) are quite large.

Thus the Hammett substituent constant was not universally applicable. Because of this, Jaffé[3] proposed that σ be redefined as "the value which best fits the entire body of experimental data." McDaniel and Brown[6] disagreed with Jaffé and suggested that it is more desirable to have unambiguous values of the substituent constant, together with their estimated precision. Jaffé's approach is more useful for the simple correlation of data, but it makes the data less useful for other purposes. If the data are to be used for theoretical studies, such as the separation of the inductive and resonance components of Hammett substituent constants, the analysis of factors which influence the observed effects of substituents or for discussions concerning deviations from the Hammett equation, unambiguous values of sigma are necessary. For these reasons, a return to Hammett's original definition for the substituent constant was recommended.[6]

The three-scale system has been shown to be inadequate when applied to substituents capable of resonance, with σ values varying widely between the limiting values as represented on the σ^+ and σ^- scales. To overcome this, attempts were made to obtain substituent inductive constants, in which the resonance factor would be altogether eliminated.

Van Bekkum and coworkers[7] determined values for the reaction constant ρ, using only substituent constants which clearly did not involve resonance interactions; meta substituents and some para substituents, in which resonance effects were considered to be absent,

were used for this purpose. Other substituents were then placed on the correlation line and their resonance-free σ^n values determined. Norman[8] argued that this treatment neglected the polar effect of the substituent on the resonance interaction of the reaction centre with the aromatic nucleus and overcame this problem by insulating the functional centre from the benzene ring by an intervening methylene group. A scale of σ_G values was proposed, based upon the alkaline hydrolyses of substituted and unsubstituted ethyl phenylacetates in which the reactive acetate group is separated from the benzene ring by a $-CH_2-$ group. Taft[9] employed a similar approach. He attempted to separate inductive and resonance effects by employing reactants in which the reacting centre was separated from the benzene ring by means of a methylene group, and assumed that the resonance component of the substituent effect would be essentially constant for the reaction series. The inductive constants thus obtained were designated σ°. The three scales, σ^n, σ_G and σ°, are very similar to each other and to the Hammett scale for meta substituents; however, for para substitutents, especially those which can supply electrons by resonance interactions, differences occur even between the σ^n, σ_G and σ° scales themselves (see Table 1, Ref. 5).

Others have attempted to take into account the variations in conjugative effects, rather than exclude them, by introducing a factor, r, which is a measure of a degree of resonance relative to the limiting cases requiring σ^+ or σ^-. Factor r is constant for a given reaction series but may vary from series to series. Two equations have been proposed which apply to positive and negative reaction sites

respectively:

$$\log k/k_o = \rho[\sigma + r\ (\sigma^+ - \sigma)]^{10} \qquad [5]$$

and $$\log k/k_o = \rho[\sigma + r\ (\sigma^- - \sigma)]^{11} \qquad [6]$$

The former equation, using $r = 0.5$, has been used by Dessy and coworkers to correlate the rates of some diaryl mercury compounds.[12]

A different approach to the problem of variable resonance contributions of the substituents has been described by Hine.[13,14] The assumption that ρ (meta) and ρ (para) need not necessarily be equal led to the development of an expression which showed that σ and ρ are not independent of one another. In the reaction $ArX_1 \rightleftarrows ArX_2$, in which the σ values of substituent groups X_1 and X_2 can be fitted to the Hammett equation, ρ_x was shown to be proportional to the differences between the σ constants of X_1 and X_2:

$$\rho_x = \tau(\sigma_{x_1} - \sigma_{x_2})$$

The proportionality constant, τ, is independent of the nature of the reaction but is dependent upon reaction conditions and is said to be a measure of the efficiency of the transmission of the influence of the substituent to the reaction centre under specific experimental conditions. As with the Hammett equation, however, the unmodified equation was not able to satisfactorily correlate data of para substituents in which the resonance interaction between the reaction centre and the ring changes substantially during the reaction. It was found to be necessary to introduce a resonance term, σ^R, into the

equation for the free energy of polar interaction of para substituted compounds. Thus:

$$\log (k/k_o) = \sigma_p \rho_p + (\sigma_x^R \sigma_y^R) \qquad [8]$$

where σ_x^R and σ_y^R are resonance substituent constants for the substituent and for the reaction sites respectively. On the basis of this approach, Hine[14] has evaluated σ^R values for a number of meta and para substituents.

Substituent effects in aliphatic systems, excluding hyperconjugation, cannot involve resonance interactions and Hammett's σ is generally not applicable to such systems. However, the reactivities of 4-substituted bicyclo [2.2.2] octane-1-carboxylic acids were found to be of comparable magnitude to those of meta and para substituted benzene derivatives.[16] Taft[15,17] defined a set of polar substituent constants, σ^*, for use in aliphatic systems, on the basis of the acid and base catalysed hydrolyses of ethyl esters of substituted acetic acids:

$$\sigma^* = \frac{1}{2.48}\left[\log \frac{k}{k_o}_{\text{base}} - \log \frac{k}{k_o}_{\text{acid}}\right] \qquad [9]$$

where k is the rate constant for the hydrolysis of an ethyl ester having the formula $RCOOC_2H_5$ and k_o that of the standard ester, R = Me. These values were used in an equation analogous to the Hammett equation:

$$\log k/k_o = \sigma^* \rho^* \qquad [10]$$

Even though the Taft equation was proposed for a series of

aliphatic compounds, it has, on occassion, been applied to aromatic series; conversely, the Hammett equation has, on occasion, been applied to aliphatic series. Thus the equations overlap in their application. (Some examples of this are to be found in Ritchie and Sager's review article).[5]

Taft[18] proposed that the Hammett σ be quantitatively separated into independent inductive, σ_I, and resonance, σ_R, factors. That is:

$$\sigma \equiv \sigma_I + \sigma_R \qquad [11]$$

The new scale of substituent constants, σ_I, was assumed to be a measure of the inductive contribution of substituents to the Hammett σ constants for both meta and para substituents (excluding charged substituents). σ_I was related to σ^* by the equation:

$$\sigma_I = 0.45\,\sigma^* \qquad [12]$$

where 0.45 is a normalization constant.

Thus a number of substituent constant scales are available, some of which do not differ significantly from one another. These scales were compared by Ritchie and Sager.[5] The authors recommended that only the σ_I, σ, σ^-, and σ^+ symbolism be retained, except for those substituents which either bear a formal electronic charge or which are, at the same time, strongly electron-withdrawing and resonating. With these few exceptions, the σ, σ°, σ^n, σ_G and σ^R scales are identical within the limits of experimental error and the σ^* scale is simply related to σ_I.

1.2 The Reaction Constant

The Hammett equation yielded the reaction constants, ρ, as proportionality constants dependent upon the response of a reaction series to changes in the substituent, relative to a standard reaction. The interpretation of substituent constants, σ, as measures of the polar effects of substituents leads to the identification of reaction constants as measures of the susceptibility of the reacting group to electrostatic and electronic effects. The overall susceptibility is a function of (a) the transmission of electrical effects to the reaction site, (b) the response of the reaction to changes in electron density at the reaction site and (c) the effect of reaction conditions. Reactions with positive ρ values are facilitated by low electron density and those with negative ρ values by high electron density at the reaction site.[3] Two basic assumptions concerning the nature of reaction constants have been accepted by most authors: (i) reaction and substituent constants are independent of one another and (ii) reaction constants are a characteristic of a particular reaction series under specific conditions of temperature and solvent and are applicable to both meta and para substituents alike. Hine[13,14] questioned the validity of the practice of applying the same ρ values to substituents in both meta and para positions, and assumed that ρ values for meta and para substituents need not necessarily be equal. A statistical examination of more than 300 reaction series[19] supported Hine's conclusions, but it also indicates that only a few systems require separate ρ values for the meta and para positions. In 85% of the series included in the study, there was no significant difference between ρ(meta) and

ρ (para). Only a few series showed serious differences which, in part, may have been due to the inclusion of data of many para-substituted compounds having enhanced σ values.[26]

The application of Hine's treatment is also limited to equilibrium systems of the type:

$$ArX_1 \rightleftharpoons ArX_2 \qquad [13]$$

where the σ values of X_1 and of X_2 are known. The reaction constant for the system is proportional to the difference between the σ constants for X_1 and X_2. It is not possible to apply the treatment to reaction rates, since X_2 would then correspond to a transition state, the structure of which would be largely speculative and for which σ values would be unknown.

Ritchie and Sager[20] also derived a relationship between the reaction constant, ρ, and the substituent constants of the groups involved in reactions which are not complicated by variable resonance or by steric interactions:

$$\rho = \alpha^2(\sigma_{r1} - \sigma_{r2})/T \qquad [14]$$

where r1 and r2 refer to the substituents exchanged in the course of the reaction and α is the proportionality constant.

1.3 Applications of the Hammett Equation

The Hammett equation in its original form applied to derivatives of benzene in which substituent groups were situated meta or para to a reacting side-chain, and in which there was no direct conjugation between the substituent and the reacting group. Within these limitations

the equation was used to correlate satisfactorily both equilibrium and rate data, even though the former is independent and the latter completely dependent upon the reaction path between reactants and products. However, rate data is only successfully accommodated if there is no change in the mechanism of the reaction within the series; should such mechanistic changes occur abrupt changes in ρ values often result. A different ρ will apply to each mechanism. Conversely a Hammett plot which demonstrates a sudden break in the correlation line is often interpreted as being the result of a change in mechanism within the series under study. Thus, sudden changes in ρ-values within a series of Schiff bases have been interpreted in terms of mechanistic changes due to a change in the structure of the reacting molecule from a planar to a non-planar configuration[38,73] or due to solvent-solute interactions.[79] In general, uncertainty concerning the structure of transition states make correlations involving rate data less satisfactory than those involving data from equilibria only because, in the latter, the reactants and products are generally well defined.

The Hammett equation was unsatisfactory for the correlation of the rate or equilibrium data of compounds in which powerful electron-donating and electron-withdrawing substituents were in direct conjugation with the reacting centre, and the equation was extended to include these groups by determining special σ^+ and σ^- values respectively, which would apply to these compounds. Thus σ^+ values are used to correlate data from electrophilic reactions and σ^- is applied to nucleophilic reactions. In many instances, conclusions as to the nature of transition

states have been based on whether the data obtained correlates best with σ, σ^+ or σ^-, though Ritchie and Sager[5] warn that such deductions may be unreliable. The Hammett equation should also be valid for aromatic and heteroaromatic systems which have substituent and reacting group in meta and para positions relative to one another since these, like benzene, are planar and rigid. When considering a substituted benzene ring in a fused ring system, however, the situation is complicated in that the adjacent ring is attached to the ring bearing the substituent in two positions. A modified form of the Hammett equation has been applied to such situations:[3,21]

$$\log k/k_o = \sigma_1\rho_1 + \sigma_2\rho_2 \qquad [15]$$

where $\sigma_1\rho_1$ and $\sigma_2\rho_2$ refer to the two points of attachment. An alternative approach selects the parent (unsubstituted) compound of a given series as a standard. Thus σ_N values are reported for the naphthalene system.[5] The use of the Hammett equation was further extended in its application to saturated ring systems, such as the rigid 4-substituted biclo[2,2,2]octane-1-carboxylic acid system.[16] In this system the carbonyl group and the 4-substituent are approximately the same distance apart as in the para substituted benzoic acid series and, because of the absence of electronic effects, the system was used to estimate inductive reaction constants for the substituents. The equation $\log k/k_o = \sigma'\rho'$ is followed in this system.

A variety of other data has also been successfully correlated by means of the Hammett equation.[22(a),24,26] It has been widely applied to polarographic reduction potentials[23,25,54] and this is not

unexpected because reduction potentials are essentially measures of equilibrium constants. (This is discussed in more detail in Chapter 3). The correlation of substituent constants with spectroscopic data, including nuclear magnetic resonance (n.m.r) and ultraviolet and infrared spectra and mass spectroscopy,[86] have been summarised by Wells.[26]

Streitweiser applied free energy relationships to electrophilic substitution in polynuclear hydrocarbons[22(a)] and found that for a particular substitution reaction, the relative reactivities of reaction sites correlated with their basicities. In this treatment the nature of the attacking reagent was neglected since it was the same for all the hydrocarbons considered. The variations in the reactivities of the various positions in the aromatic nucleus were considered in terms of the localisation energies at these positions. An equation, analagous to that of Hammett, was proposed for electrophilic substitution reactions in polynuclear hydrocarbons:

$$\log k_r/k_{\alpha\text{-naphth.}} = \sigma_r \rho^* \qquad [16]$$

where the standard substitution reaction is the protonation equilibrium and $\rho^* = 1$ for this reaction; σ_r then gives a direct measure of the relative basicity of the position, r, in any aromatic hydrocarbon. The 1-naphthalene position was chosen as the reference position for reasons of convenience and accuracy. These σ_r values have been correlated with a number of properties of the hydrocarbon molecules, including spectral properties, polarographic half-wave potentials, electron ionisation potentials, and theoretical energies of the lowest

unoccupied and highest occupied molecular orbitals.[22,24]

Maccoll[25] showed that the polarographic half-wave reduction potentials of several aromatic hydrocarbons are linearly correlated with the energies of the lowest vacant MO's of the hydrocarbons and others have confirmed and interpreted these observations.[27,29] However, it was noted that compounds that are non-planar, e.g. 9,9'-dianthryl (in which the two groups are at approximate right angles to one another), do not fit the correlation.[22(b),28] Scott and Jura[54] extended this treatment to Schiff bases of the type ArCH = NAr' and correlated the half-wave potentials of these compounds with the energies of the highest occupied and lowest unoccupied orbitals. The energies were calculated by the linear combination of molecular orbital (l.c.m.o.) variant of the Huckel molecular orbital theory. Schiff bases were used instead of the analogous hydrocarbons because of the relative ease of preparation of the former. However, while making the synthetic problem easier, some theoretical problems were introduced which were neglected by (a) assuming that the Schiff bases were planar and in the trans-configuration and (b) applying the l.c.m.o. perturbation method without specific consideration of the heteroatom present. It was also assumed that both the mechanism of the reduction process and solvation terms were invariant with structure.

The structure of Schiff bases has been the subject of much discussion (this is discussed in more detail in Chapter 2) and it has been shown that Schiff bases are almost certainly not planar, but that the molecules are twisted about the N-Ar bond, due to the interaction of the unshared pair of electrons on the nitrogen atom with the

π-electrons of the aromatic system. Despite the fact that the non-planar 9-9'-dianthryl does not fit the correlation described above, Scott and Jura[54] obtained some impressive correlations with the non-planar Schiff bases.

Dewar[83,84] has described the effects of substituents in terms of two factors, one being the electron density at the point of attachment of the substituent (which, for odd alternant hydrocarbons, can be determined by nonbonding molecular orbital (n.b.m.o.) calculations) and the other being some measure of the activity of the substitutent. He has emphasized, however, that the quantitative measurements necessary to test this approach are not available and that it is necessary to have extensive and reliable measurements of substituent effects in aromatic systems other than benzene. The present project provides an extensive systematic series of measurements of substituent effects in large conjugated systems.

The present project further extends the investigation of the polarographic reduction of aromatic Schiff bases and the correlation of their half-wave potentials by means of linear free energy relationships. Six series of Schiff bases, each containing 19 compounds, have been prepared and their half-wave potentials measured in dimethylformamide. The electro-reduction process corresponding to the first polarographic wave involves a very simple chemical reaction, namely the addition of one electron to the π-system of the Schiff base. Complications of this essentially simple process have been reduced to a minimum by using carefully dried and purified dimethylformamide, which avoids the possibility of the rapid protonation of the reduction product. The use

of large reactant (Schiff base) molecules also reduces solvation effect variations to a minimum (solvent effects are discussed in greater detail in Chapter 3).

CHAPTER 2

THE STRUCTURE OF SCHIFF BASES

The planar configurations of trans-stilbene (Fig. 2.1) and trans-azobenzene (Fig. 2.2) have long been established on the basis of their crystal structures.[36,37] More recently, absorption bands in trans-stilbene (λ_{max} 2950 Å)[30,42] and in trans-azobenzene (λ_{max} 3150 Å)[42] have been attributed to the overall conjugation occurring in these molecules. A similar band appears in the spectrum of the isoelectronic benzalaniline (λ_{max} 3150 Å)[30,42] but the intensity of the band in the Schiff base (E_{max} 8000) is much less than that in the spectra of trans-stilbene (E_{max} 28,000) and azobenzene (E_{max} 23,000). This is but one of a number of properties of Schiff bases which differs from those of their isoelectronic analogues;[43] in addition Schiff bases of the type ArCH=NAr' are less basic and are non-luminescent, and their cis-isomers have not been isolated.[33]

Ismailski and Smirnov[31] recognised that conjugation in benzalaniline was less than in stilbene and postulated that the unshared pair of electrons on the nitrogen atom in benzalaniline are conjugated with the π-electron system of the N-phenyl ring. Such a model implies an acoplanar structure because, to permit such an interaction, it is necessary for the molecule to be twisted along the N-phenyl bond, thus bringing the orbital of the nitrogen lone pair electrons into the plane of the π system of the ring. This restricts the overall π-conjugation in the molecule and accounts for the observed reduction in the intensity of the band at λ_{max} = 3100 Å. In Schiff bases prepared from aniline

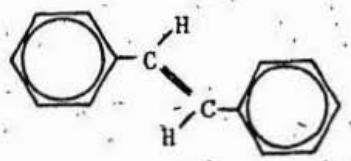


Fig. 2.1 Trans-stilbene

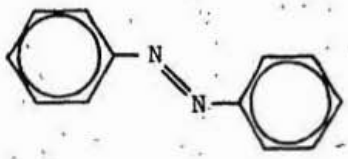


Fig. 2.2 Trans-azobenzene

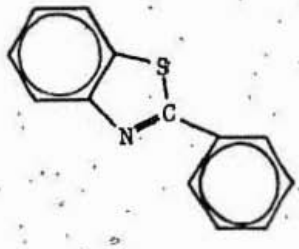


Fig. 2.3 2-phenyl-benzothiazole

and aliphatic aldehydes, this same absorption band (at λ_{max} = 3100 Å) is absent altogether.[44] Ebara,[43] on the basis of ultraviolet spectral evidence, also concluded that the benzylidene-aniline molecule was non-planar, and suggested that the ring of the aniline portion was almost perpendicular to the rest of the molecule.

Localization of the nitrogen lone pair electrons by nitrone formation,[30] by N-methylation[44] and by protonation[30,44] effectively removed the possibility of conjugation between the orbital of the nitrogen lone pair and the N-phenyl ring. Products were obtained in which the intensity of the band at λ_{max} = 3100 Å was considerably increased,[30] [E_{max}(nitrone) = 20,000; E_{max}(protonated species) = 19,500]. In addition, compounds in which the -N = C- linkage was fixed as part of a 5-membered ring, for example, 2-phenyl benzothiazole (Fig. 2.3), in which the benzalaniline skeleton was made to assume a planar configuration, all gave spectra comparable to that of trans-stilbene.[30] These conclusions were substantiated by W. F. Smith,[45] who studied the ultraviolet absorption spectra of a series of increasingly hindered Schiff bases and showed that as hindrance to planarity was increased, the extinction coefficient of the peak at λ_{max} = 3100 Å decreased. (At the same time there was an increase in the extinction coefficient of the peak at λ_{max} = 2620 Å).

The weakening of the overall π-conjugation in the molecule due to acoplanarity would be expected to lead to some measure of independence of the aldehyde and amine portions of the molecules and to the appearance of bands corresponding to these components in the spectrum.[43] Indeed, a shorter wavelength band does occur in benzalaniline (λ_{max} = 2560 Å;

E_{max} = 16,200) in approximately the same position as a similar band in benzaldehyde methylimide (λ_{max} = 2460 Å; E_{max} = 19,400) and it was proposed that these bands have a common origin in the benzal portion of the respective molecules.[30] (The displacement of λ_{max} by 100 Å in benzalaniline was attributed to the inductive effect of the terminal phenyl ring). Anils of acetophenone have two absorption maxima, at λ_{max} = 2500 Å and at λ_{max} = 3100 – 3200 Å, which have been assigned to the contributions of the ketone and amine components respectively. The introduction of substituents into the ketone ring led to distinct shifts of the ketone band (λ_{max} = 2500 Å) and to much smaller shifts of the amine band while substituents in the amine ring had a much greater influence on the wavelength of the amine band at λ_{max} = 3100 – 3200 Å than on that of the ketone band, which remained virtually unchanged.[32] Similar results were obtained by Ebara.[44]

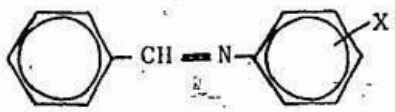
The acoplanar model was supported on theoretical grounds by Minkin et al.,[33] who showed that variations in the dihedral angle (θ) between the plane of the amine nucleus and that of the remainder of the molecule had little effect upon the calculated delocalization energies of the various conformers, because of mutual compensation between the π–π and n–π interactions. Under these conditions steric factors were thought to be critical in determining the stable conformation of the molecule and thus the effect of changes in θ upon the repulsion energy between the hydrogen atom of the azomethine group and the ortho-hydrogen of the amine ring were determined. The combined delocalization and repulsion energies indicated that the most stable configuration was that in which θ was between 40° and 60°. This result was substantiated

by applying the formula $\cos^2\theta = \varepsilon/\varepsilon^\circ$,[34] where ε and ε° are the molar extinction coefficients of compounds with non-planar and planar configurations respectively. Values of θ ranging from 43° to 64° were obtained for substituted benzalanilines.

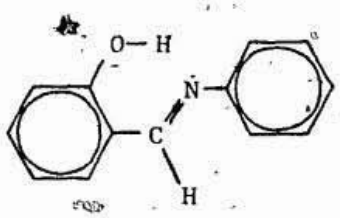
However, Houlden and Csizmadia[35] assumed a planar model of benzalaniline in which both the C_6H_5-N = C and C_6H_5-C = N angles were kept at 120° and calculated that a 5° rotation of the phenyl ring of the aniline portion of the molecule would lower the energy of the molecule by only 0.3 kcal/mole. This was not considered to be large enough to justify an acoplanar model. The authors therefore assumed planar geometry throughout and ascribed the anomalies to the opening of the C_6H_5-N = C angle. Optimum values for the C_6H_5-N = C and C_6H_5-C = N angles were calculated to be 156° and 128° respectively, and that of the C_6H_5-C-H angle was shown to be 116°.[35] The transition energies of five benzal-p-X-anilines, predicted by an extended Hückel treatment, were used as a guide for least squares resolution of the observed ultraviolet spectra of these compounds. The comparison of the resolved and predicted spectra permitted a one-to-one assignment of the bands. This technique indicated the presence of a band under the tail of the first $\pi^* \leftarrow \pi$ band, corresponding to the first $\pi^* \leftarrow n$ band. The presence of this band favours the planar model since, in the acoplanar configuration, the nitrogen atomic orbital conjugates with the ring electrons, and the band would disappear. Good correlations of the $\pi^* \leftarrow \pi$ band shifts of the substituted compounds, relative to benzalaniline, with other substituent properties were claimed to be an indication of the reliability of this method.[35] No correlations were

found with Hammett's σ_p values in this study, in agreement with the failure of half-wave potentials of benzal-p-X-aniline compounds to correlate with σ_p.[31]

Evidence concerning the structure of Schiff bases has also been forthcoming from basicity measurements. Korolev et al.,[38,39] plotted pK_a values, measured in acetonitrile, against Hammett's σ constants for a series of substituted compounds of general formula:



Two lines were obtained, intersecting at X = H. For nucleophilic substituents the ρ_n value was 2.26, while for electrophilic substituents a ρ_e value of 3.91 was obtained, which is very close to the value for anilines (ρ = 3.81). A similar plot with compounds of general formula:



in which the molecule is constrained in a planar configuration, resulted in a straight line plot with ρ = 2.11, which is very similar to ρ_n. On the basis of these results it was proposed that those Schiff bases with an electrophilic group (ρ = 3.9) were non-planar, (c.f. anilines,

ρ = 3.81) while those with nucleophilic group (ρ = 2.26) were planar, like the o-hydroxybenzilidine compounds (ρ = 2.11).

More recently, nuclear magnetic resonance studies of Schiff bases[40,41] have supported the non-planar model. Tabei and Saiton[40] compared the effects of para substituents in each ring on the signal of the azomethine proton and on the C = N stretching frequency. They showed that substituents in the para position of the aniline ring have little effect upon the azomethine group, whereas para substituents in the benzaldehyde ring have a much larger effect. This suggests that the para position of the aniline ring is not conjugated to the azomethine group. This is in agreement with the non-planar model of these molecules. Gil and Saraiva[41] observed that the chemical shifts of the two ortho protons of the aldehyde ring (adjacent to the azomethine function) were the same and so were those of the corresponding protons of the amine ring; thus both phenyl rings appear to be rotating rapidly about the bonds by which they are attached to the azomethine group. The authors[41] thus talked in terms of 'average' or 'weighted' dihedral angles and showed this was a maximum of 45° for the aniline ring.

CHAPTER 3

THE POLAROGRAPHY OF SCHIFF BASES

3.1 Solvent Effects

Early investigators of the polarographic behaviour of Schiff bases used aqueous-alcohol solutions but any theoretical interpretation of the results thus obtained would likely be of doubtful value, since the half-wave potentials thus measured are unreliable.[51] Three factors have been shown to be important in this regard.

(i) Schiff bases are readily hydrolysed, even by water, to the parent amine and aldehyde[80,81] and, under aqueous or partially aqueous conditions, an equilibrium mixture of Schiff base, aldehyde and amine is often present.[74]

(ii) The presence of proton donors would likely influence the nature of the electrode reaction, making it much more likely that rapid protonation would occur. The presence of proton donor species has been shown to have an effect upon the mechanism of the electro-reduction of aromatic hydrocarbons.[46-51] Significant changes were observed in the values obtained for the half-wave potentials ($E_{\frac{1}{2}}$) and for the limiting current when changes were made in the concentrations of electro-inert proton donors present. Measurements of the variation of $E_{\frac{1}{2}}$ for the reduction of 4,5-methylene-phenanthrene (Fig. 3.1) in dimethylformamide with increasing concentration of added proton donor (phenol) showed that the change in $E_{\frac{1}{2}}$ with ArOH is greatest in the low

concentration range of the proton donor; thus even small concentrations of proton donors were shown to cause significant errors in the measurement of true $E_{\frac{1}{2}}$ values of aromatic hydrocarbons.[51] It is to be expected that Schiff bases would react to the presence of proton donors in a similar fashion, and evidence of this has been reported.[78]

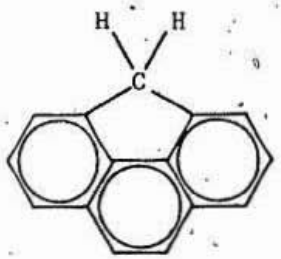


Fig. 3.1 Methylenephenanthrene

(iii) Solvation might play an important part when aqueous alcohol is used as the reaction medium. Bezuglyi et al.,[79] compared $E_{\frac{1}{2}}$ values of substituted N-benzylideneanilines measured in aqueous alcohol, sulfuric acid and dimethylformamide respectively and correlated the values obtained with Hammett σ values. Straight line correlations resulted when half-wave potentials determined in dimethylformamide or in sulfuric acid were used, but a broken curve was obtained when the half-wave potentials determined in aqueous alcohol were correlated with σ. It was proposed that the Schiff base molecules were hydrogen-bonded to both water and alcohol in the aqueous alcohol medium through the nitrogen lone pair electrons; this ability to hydrogen bond

is even more marked when electron-donating substituents are present in the molecule. The authors[79] suggest that, in proton-donating solvents (alcohol, water), the group reduced at the electrode in the hydrogen-bonded species, $-CH = N- \cdots H$, differs significantly from that reduced in the non-bonded species, $-CH = \ddot{N}-$. The solvent therefore contributes to a change in the nature of the reaction centre, though this is also influenced by the substituent present. For the correlation of the $E_{\frac{1}{2}}$ values measured in aqueous ethanol the two ρ values obtained from the broken curve reflect this change in the reaction centre. In aprotic solvents, however, such a change in the electroactive group is not possible and straight line correlations are obtained.[79]

However, in a reaction series in which neither the reaction site nor the reaction mechanism is subject to such solvent-induced variations, other solvent effects can be neglected.

The influence of solvation energies is apparent from the following thermodynamic cycle:

$$\begin{array}{lcll} \text{Ar-CH = N-Ar'} + \bar{e} & \xrightarrow{E_f} & \text{Ar-}\bar{\text{C}}\text{H-}\dot{\text{N}}\text{-Ar'} & \text{(in gas phase)} \\ \delta_e G_N \uparrow\downarrow & & \delta_S G_{RA} \uparrow\downarrow & \\ \text{Ar-CH = N-Ar'} + \bar{e} & \xrightarrow{\Delta G_s} & \text{Ar-}\bar{\text{C}}\text{H-}\dot{\text{N}}\text{-Ar'} & \text{(in solution)} \end{array}$$

where $\delta_e G_N$ is the free energy of the transfer of a neutral molecule

from solution to the gas phase, E_f is the electron affinity of the neutral molecule in the gas phase. $\delta_S G_{RA}$ is the free energy of solvation of the gaseous radical anion and ΔG_s the free energy of addition of an electron to the neutral molecule in solution. A further set of terms appropriate to taking the reference electrode-electron system around the cycle is not included because these are essentially constant throughout any reaction series and is represented in equation [17] by the constant term C:

$$\Delta G_s = \delta_e G_N + E_f + \delta_s G_{RA} + C \qquad [17]$$

The half-wave potential, $E_{1/2}$, for a reversible one-electron reduction is given by the equation:

$$E_{1/2} = \frac{\Delta G_s}{F} - \frac{RT}{F} \log \frac{D_N}{D_{RA}} \qquad [18]$$

where F is the Faraday and D_N, D_{RA} are the diffusion coefficients of the neutral molecule and radical anion respectively.[22(b),27] Assuming that $D_N = D_{RA}$,[22(b)] equation [18] becomes:

$$E_{1/2} = \Delta G_s / F \qquad [19]$$

The half-wave potential is thus proportional to ΔG_s. Substituting the value for ΔG_s into equation [17] we have:

$$F E_{1/2} = \delta_e G_N + E_f + \delta_s G_{RA} + C \qquad [20]$$

If we assume that solvation terms are invariant with structure, i.e. $\delta_e G_N$ and $\delta_s G_{RA}$ remain constant throughout a series and are not subject to substituent effects. Thus:

$$E_{\frac{1}{2}} = \frac{E_f}{F} + C' \qquad [21]$$

Variations in $E_{\frac{1}{2}}$ for a reaction series are thus proportional to variations in the electron affinity of the molecules in the gas phase, and are not influenced by solvation energies. This equation is the starting point for relating the half-wave potential for the first polarographic wave to theoretical quantities obtained from quantum mechanical calculations. Correlations of the energies of the lowest unoccupied and highest occupied molecular orbitals with polarographic reduction potentials and ionisation potentials have been frequently reported.[22(b),24,55]

3.2 Relation between Half-wave Potentials and Substituent Effects

The electrical work performed during an electrolytic reduction is accompanied by an increase in the free energy of the system equal to the net electrical work performed:

$$\Delta G = nFE \qquad [22]$$

where ΔG is the increase in free energy and n the number of electrons involved in the reduction process at potential E and F is the Faraday.

For a reversible process, the standard free energy change, ΔG°, at the half-wave potential, $E_{\frac{1}{2}}$, is given by:

$$\Delta G^\circ = nFE_{\frac{1}{2}} \qquad [23]$$

Furthermore, for a reaction at equilibrium, the standard free energy change is related to the equilibrium constant for the reduction

process:

$$\Delta G^\circ = - RT \ln K \qquad [24]$$

Combining equations [23] and [24], we get:

$$\Delta G^\circ = nFE_{\frac{1}{2}} = -RT \ln K$$

$$\text{i.e.} \quad E_{\frac{1}{2}} = \frac{-RT}{nF} \ln K \qquad [25]$$

The half-wave potential is therefore proportional to the logarithm of the equilibrium constant. Hammett substituent constants are generally correlated with rate and equilibrium constants and it is not surprising therefore that correlations between σ-values and half-wave potentials are quite successful. In a given series of compounds the differences between the half-wave potentials of substituted, $(E_{\frac{1}{2}})_x$, and unsubstituted, $(E_{\frac{1}{2}})_o$, compound are given by:

$$\Delta E_{\frac{1}{2}} = (E_{\frac{1}{2}})_x - (E_{\frac{1}{2}})_o \qquad [26]$$

Combining equations [25] and [26] we obtain:

$$\Delta E_{\frac{1}{2}} = \frac{RT}{nF} \ln K', \text{ where } \ln K' = \ln \frac{K_x}{K_o} \qquad [27]$$

The Hammett equation gives $\log K_x/K_o = \sigma\rho$. Thus, for a series of compounds which obey Hammett's empirical relationships:

$$\Delta E_{\frac{1}{2}} = - \frac{RT}{nF} \sigma\rho \qquad [28]$$

3.3 The Reaction Mechanism

The possible reaction paths for the electro-reduction of Schiff

bases are assumed to be similar to those proposed for the electro-reduction of aromatic hydrocarbons[52,71,72,53,59] (Fig. 3.2).

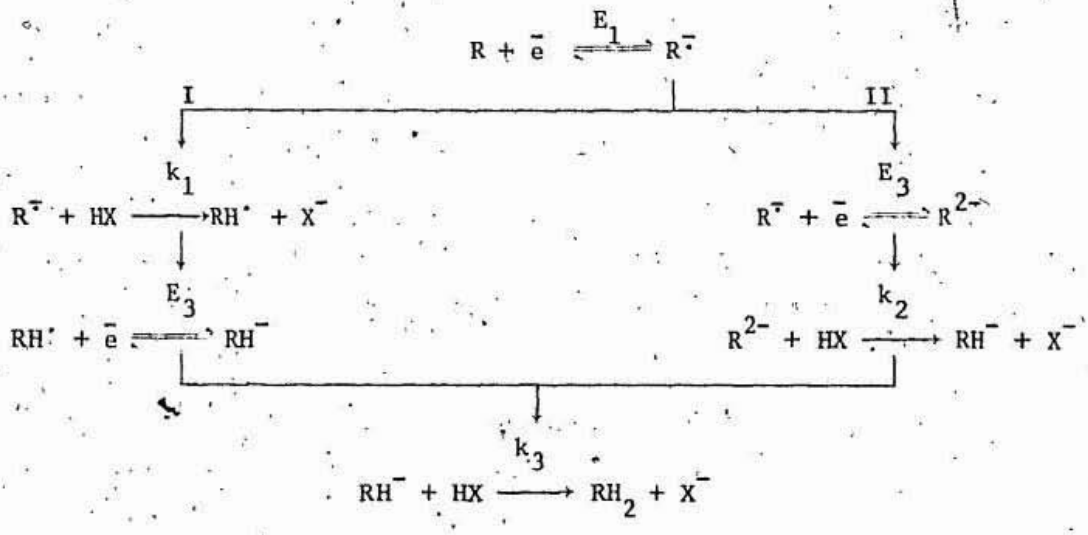


Fig. 3.2 Possible Reaction Paths for the Electro-reduction of Schiff Bases

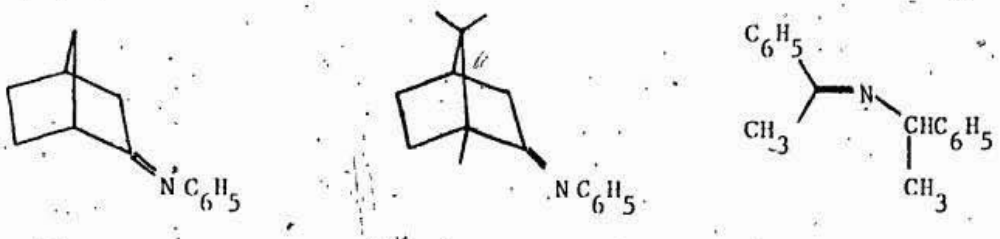
The factor governing the reaction path followed is the rate of protonation of R^- which, in turn, depends upon the product $k_1[HX]$, where HX is a proton donor. In the presence of high concentrations of proton donors, reaction path I is favored; the lifetime of R^- would likely be very short and the radical anion would be rapidly protonated. This reduction mechanism would manifest itself as a single reduction wave corresponding to a two-electron transfer.[52] The value of k_1 would depend upon the basicity of the imine radical anion, R^-. Consequently, k_1 would be expected to vary considerably with the structure of the radical anion produced.

The Schiff bases studied by Fry and Reed[52] (Fig. 3.3) are apparently reduced by mechanism I (Fig. 3.2) since a single two-electron

transfer is involved. This is so despite the fact that these compounds were reduced in dimethylformamide which had been carefully dried and purified. The authors suggested that the tetraalkylammonium salt used as the backing electrolyte was itself acting as a proton donor by undergoing a Hofmann elimination reaction:

$$(CH_3CH_2)_4N^+ \rightarrow (CH_3CH_2)_3N + CH_2 = CH_2 + H^+ \qquad [29]$$

The authors report that this reaction occurs quite rapidly in dimethylformamide.[52]



(a) (b) (c)

Fig. 3.3 Schiff Bases Studied by Fry and Reed[52]

Fry and Reed predicted, however, that highly phenylated radical anions would be more stable than those produced from (a) - (c) in Fig. 3.3, because of resonance stabilisation; this was confirmed by the electroreduction of $(C_6H_5)_2C = N\text{-}C_6H_5$, which was reduced to a stable radical-anion by means of a reversible one-electron transfer.[52] Electron spin resonance (e.s.r.) spectra have been used to detect the presence of

free radicals for N-benzylidenesulfanilamide[78] and $C_{10}H_7-N=CH-C_{10}H_7$.[54]

The electro-reduction of aromatic hydrocarbons and ketones in dimethylformamide follows pathway II (Fig. 3.2); two well defined waves are observed, corresponding to the addition of two electrons in two discrete one-electron transfers. Similar waves were also obtained in the reduction of a variety of Schiff bases,[54,74-8] the diffusion current (i_d) values of which were similar in magnitude to those obtained in the reduction of aromatic hydrocarbons.[54,55] This favourable comparison suggests that aromatic Schiff bases are usually reduced by reaction path II (Fig. 3.2), though those derived from ortho- and para-hydroxyaniline show some anomalous behaviour.[77]

Further evidence has been reported in favour of the two-stage addition of electrons in Schiff bases: (reaction path II in (Fig. 3.2))

(i) Re-oxidation of the first reduction stage was observed using cyclic voltametric techniques.[54]

(ii) Large scale electro-reduction of N-benzylidenesulfanilamide and of N-benzylideneaniline conducted at their half-wave potentials led to the formation and isolation of products of double molecular weight.[78] The dimers, which were identified on the basis of infrared spectra and cryoscopic measurements, were probably formed according to the scheme:

$$2\left[C_6H_5CH-N-C_6H_5\right]^{\cdot-} \rightarrow \begin{matrix} C_6H_5-CH-\bar{N}-C_6H_5 \\ | \\ C_6H_5-CH-\bar{N}-C_6H_5 \end{matrix} \xrightarrow{2H^+} \begin{matrix} C_6H_5-CH-NH-C_6H_5 \\ | \\ C_6H_5-CH-NH-C_6H_5 \end{matrix} \quad [30]$$

On the basis of this evidence and following the example of previous workers,[54,74-8] it is assumed in this project that the aromatic

Schiff bases being studied are reduced by mechanism II (Fig. 3.2). The first polarographic wave recorded thus corresponds to a reversible one-electron transfer, leading to the formation of a stable radical anion.

CHAPTER 4

EXPERIMENTAL.

4.1 Preparation of Schiff Bases

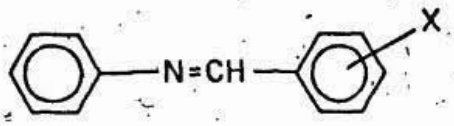
Six series of Schiff bases, each of nineteen compounds, and having the structures shown in Fig. 4.1 were prepared.

General Procedure

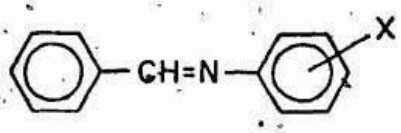
Equimolar amounts of the parent amine and aldehyde were dissolved in 95% ethanol (ca. 25 ml.) or dry benzene, the latter being used when the starting materials were insoluble in ethanol or when the product failed to form in ethanol, possibly because of hydrolysis. When necessary a small quantity of catalyst (p-toluenesulfonic acid) was also added. The reaction mixture was refluxed for about one hour, with molecular sieves being added when benzene was used as solvent. The majority of the products were crystalline and these were recrystallised from a suitable solvent, usually aqueous ethanol or benzene petroleum ether, until a constant melting point was obtained. Oily products were refluxed in the solvent with decolorising charcoal, then separated and left to stand in a refrigerator. Those products which crystallised under these conditions were carefully recrystallised from a suitable solvent, usually petroleum ether with a minimum of benzene added. Oils were redistilled under vacuum and the portion of the distillate collected at constant boiling point was retained. Yields were generally satisfactory.

Descriptions of the Schiff bases, their melting or boiling points and their analytical and theoretical compositions are recorded in Tables I to VI. Spectral data are recorded in Tables VII to XII. Melting points were measured on a Fisher-John melting point apparatus and are uncorrected. Ultraviolet spectra were recorded on a Unicam SP. 800D Ultraviolet Spectrophotometer.

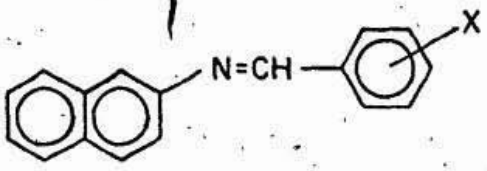
Series A



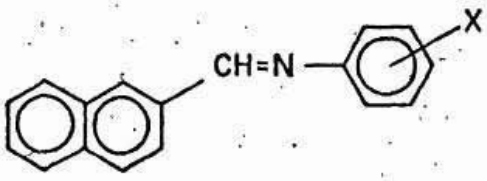
Series B



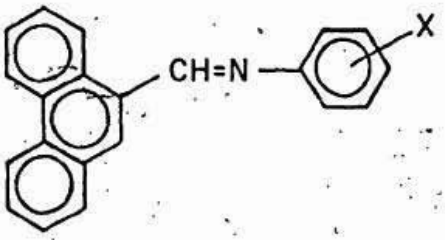
Series C



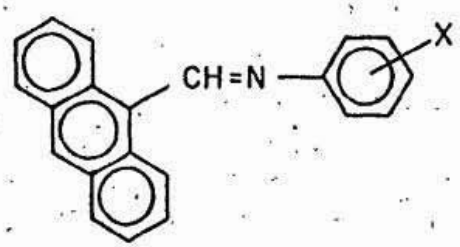
Series D



Series E



Series F



Compound No.	X
1	H
2	m-F
3	p-F
4	m-Cl
5	p-Cl
6	m-Br
7	p-Br
8	m-I
9	p-I
10	m-CH_3
11	p-CH_3
12	m-C_2H_5
13	p-C_2H_5
14	m-OCH_3
15	p-OCH_3
16	m-NO_2
17	p-NO_2
18	m-CN
19	p-CN

Fig. 4.1 Series of Schiff Bases Prepared

Table I

Physical Data of Schiff Bases in Series A ($ArN{=}CHC_6H_4X$; $Ar{=}C_6H_5$)

Compound No.	Substituent X	b.pt°/ m.pt. °C	Lit. m.pt. °C (ref)	Composition Atom: Found (calculated)	Recrystallised from	Description of product
1	H	49	52-53° (40)	C86.07(86.18); H5.98(6.08); N7.70(7.73).	95% ethanol	Pale yellow needles
2	m-F	30.5-31		C78.28(78.38); H5.10(5.02); N7.17(7.03); F9.76(9.55);	pet ether	Yellow crystals
3	p-F	41.5-42		C78.35(78.38); H5.13(5.02); N6.87(7.03); F9.59(9.55);	aqu. ethanol	White needle-like crystals
4	m-Cl	135-136°/.2 mm		C72.22(72.40); H4.62(4.64); N6.43(6.50); Cl16.28(16.48);		Lemon oil
5	p-Cl	63-63.5	63.5-64.5 (40)	C72.26(72.40); H4.76(4.64); N6.42(6.50); Cl16.33(16.48);	95% ethanol	Pale yellow plates
6	m-Br	130-134°/.3 mm		C60.00(59.99); H3.76(3.85); N5.50(5.38); Br30.61(30.77);		Yellow oil
7	p-Br	72.5-75	73-74 (40)	C59.85(59.99); H4.00(3.85); N5.19(5.38); Br30.77(30.77);	aqu. ethanol	Almost white needles
8	m-I	34.5-35		C50.61(50.81); H3.44(3.26); N4.39(4.56); I41.20(41.37);	pet ether	Yellow crystals
9	p-I	88-88.5	90-91 (40)	C50.72(50.81); H3.43(3.26); N4.37(4.56); I41.40(41.37);	95% ethanol	Pale yellow plates
10	m-CH_3	113-118°/.05 mm		C86.09(86.15); H6.80(6.67); N7.09(7.18).		Yellow oil

Table I (Continued)

Compound No.	Substituent X	b.pt.* m.pt. °C	Lit. m.pt. °C (ref)	Composition Atom: Found (calculated)	Recrystallised from	Description of product
11	p-CH_3	43.5-44	110-120* /0.1 mm (45)	C85.95(86.15); H6.79(6.67); N7.14(7.18).	95% ethanol	Pale yellow needles
12	m-C_2H_5	Not prepared				
13	p-C_2H_5	129-130* /.1 mm		C86.26(86.14); H7.02(7.18); N6.81(6.70).		Yellow oil
14	m-OCH_3	128-133* /.1 mm		C79.51(79.61); H6.35(6.16); N6.70(6.63).		Yellow oil
15	p-OCH_3	63*	63-64 (40)	C79.79(79.61); H6.21(6.16); N6.64(6.70).	methanol	White plates
16	m-NO_2	64-64.5	64.5-65 (44)	C68.85(69.03); H4.46(4.42); N12.58(12.40).	methanol	Pale yellow needles
17	p-NO_2	90.5-91	92-93 (40)	C68.91(69.03); H4.54(4.42); N12.49(12.40).	95% ethanol	Yellow needles
18**	m-CN	158-160* /.2 mm		C81.72(81.53); H4.69(4.85); N13.59(13.59).	C_6H_6/pet ether	Yellow oil
19**	p-CN	96.5-97		C81.34(81.53); H4.92(4.85); N13.41(13.59).	C_6H_6/ pet ether	Lemon yellow needles

Note. All compounds were prepared in 95% ethanol except those marked **, which were prepared in benzene.

Table II

Physical Data of Schiff Bases in Series B ($ArCH{=}NC_6H_4X$; $Ar{=}C_6H_5$)

Compound No.	Substituent X	b.pt. m.pt. °C	Lit. m.pt. °C (ref)	Composition Atom: Found (calculated)	Recrystallised from	Description of product
1	H	49	52-53 (40)	C86.07(86.18); H5.98(6.08); N7.70(7.73).	95% ethanol	Pale cream needles
2	m-F	121 /.4 mm		C78.28(78.38); H5.10(5.02); N7.17(7.03); F9.76(9.55).		Yellow oil.
3	p-F	57.5-58		C78.35(78.38); H5.13(5.02); N6.87(7.03); F9.59(9.55).	95% ethanol	Pale cream plates
4	m-Cl	37-37.5		C72.22(72.40); H4.62(4.64); N6.43(6.50); Cl16.28(16.48).	pet ether	Cream plates
5	p-Cl	60-60.5	63-63.5 (40)	C72.26(72.40); H4.76(4.64); N6.42(6.50); Cl16.33(16.48).	aqu. ethanol	Cream plates
6	m-Br	53-53.5		C60.00(59.99); H3.76(3.85); N5.50(5.38); Br30.61(30.77).	(1) ethanol (95%) (2) pet ether	Pale cream plates
7	p-Br	65.5-66	65-66 (40)	C59.85(59.99); H4.00(3.85); N5.19(5.38); Br30.77(30.77).	95% ethanol	Pale cream solid
8	m-I	65		C50.61(50.81); H3.44(3.26); N4.39(4.56); I41.20(41.37).	95% ethanol	Creamy yellow needles
9	p-I	87	85-86 (40)	C50.72(50.81); H3.43(3.26); N4.37(4.56); I41.40(41.37).	95% ethanol	Pale cream needles
10	m-CH_3	28.5-29	130-132 /1.0 mm (45)	C85.99(86.15); H6.78(6.67); N7.21(7.18).	pet ether	Pale cream plates

Table II (Continued)

Compound No.	Substituent X	b.pt.* m.pt. °C	Lit. m.pt. °C (ref)	Composition Atom: Found (Calculated)	Recrystallised from	Description of product
11	p-CH_3	32-33	122-125* /.2 mm (45)	C86.28(86.15); H6.72(6.67); N7.11(7.18).	pet ether	Pale cream needles
12	m-C_2H_5	139* /.2 mm		C86.24(86.14); H7.18(7.18); N6.58(6.70).		Yellow oil
13	p-C_2H_5	113* /.1 mm		C85.93(86.14); H6.46(7.18); N7.58(6.70).		Yellow oil
14	m-OCH_3	145* /.2 mm		C79.52(79.61); H6.31(6.16); N6.77(6.63).		Yellow oil
15	p-OCH_3	72	71-71.5 (40)	C79.48(79.61); H6.20(6.16); N6.53(6.63).	95% ethanol	Pale cream plate
16	m-NO_2	72.5-73		C68.95(69.03); H4.53(4.42); N12.43(12.40).	(1) 95% ethanol (2) C_6H_6/pet ether	Pale cream needles
17	p-NO_2	Not prepared				
18**	m-CN	41*		C81.60(81.53); H4.79(4.85); N13.51(13.59).	C_6H_6/pet ether	Pale cream solid
19**	p-CN	74-74.5		C81.41(81.53); H4.93(4.85); N13.70(13.59).	C_6H_6/pet ether	Pale yellow needles

Note. All compounds were prepared in 95% ethanol except those marked **, which were prepared in benzene.

Table III

Physical Data of Schiff Bases in Series C ($ArN{=}CHC_6H_4X$; Ar=2-naphthyl)

Compound No.	Substituent X	m.pt. °C	Lit. m.pt. °C (ref)	Composition Atom: Found (Calculated)	Recrystallised from	Description of product
1	H	99	101° (54)	C88.42(88.27); H5.50(5.68); N6.21(6.06).	95% ethanol	Cream needles
2	m-F	84-84.5		C81.73(81.90); H4.84(4.86); N5.57(5.62); F7.68(7.62).	aqu. ethanol	Cream plates
3	p-F	100-100.5		C81.71(81.90); H4.85(4.86); N5.48(5.62); F7.85(7.62).	95% ethanol	Pale pink plates
4	m-Cl	101.5-102		C76.70(76.84); H4.65(4.56); N5.32(5.27); C113.18(13.34).	(1)95% ethanol (2)C_6H_6/pet ether	Cream plates
5	p-Cl	121		C76.74(76.84); H4.64(4.56); N5.39(5.27); C113.22(13.34).	95% ethanol	Lemon plates
6	m-Br	101.5		C65.68(65.82); H4.09(3.91); N4.46(4.52); Br25.50(25.76).	95% ethanol	Cream plates
7	p-Br	124.5		C65.73(65.82); H3.95(3.91); N4.59(4.52); Br25.92(25.76).	95% ethanol	Yellow plates
8	m-I	84		C57.09(57.16); H3.44(3.39); N3.67(3.92); I35.38(35.53).	95% ethanol	Yellow plates
9	p-I	144.5-146		C56.94(57.16); H3.55(3.39); N4.01(3.92); I35.75(35.53).	(1)95% ethanol (2)C_6H_6/pet ether	Pale yellow plates
10	m-CH_3	74.5-75		C88.10(88.13); H6.32(6.16); N5.72(5.71).	(1)95% ethanol (2)C_6H_6/pet ether	Creamy-pink powder

Table III (Continued)

Compound No.	Substituent X	m.pt. °C	Lit. m.pt. °C (ref)	Composition Atom: Found (Calculated)	Recrystallised from	Description of product
11	p-CH_3	113.5		C88.10(88.13); H6.31(6.16); N5.84(5.71)	95% ethanol	Pale yellow powder
12	m-C_2H_5	Not prepared				
13	p-C_2H_5	73-73.5		C87.72(88.00); H6.41(6.60); N5.57(5.40)	pet ether	Cream powder
14	m-OCH_3	47-49		C82.91(82.75); H5.86(5.79); N5.31(5.36).	niethanol 95% ethanol	Pale yellow needles
15	p-OCH_3	97.5-98		C82.60(82.75); H5.63(5.79); N5.39(5.36)	95% ethanol	Cream plates
16	m-NO_2	91.5-92		C73.74(73.90); H4.52(4.38); N10.18(10.14)	95% ethanol	Yellow needles
17	p-NO_2	120.5-121		C73.88(73.90); H4.56(4.38); N10.33(10.14)	95% ethanol	Deep yellow needles
18**	m-CN	89.5-90		C84.36(84.47); H4.59(4.69); N16.86(10.90)	C_6H_6/pet ether	Cream-yellow powder
19**	p-CN	139.5-140		C84.25(84.47); H4.61(4.69); N10.74(10.90)	C_6H_6/pet ether	Yellow plates

Note. All compounds were prepared in 95% ethanol except those marked **, which were prepared in benzene.

Table IV

Physical Data of Schiff Bases in Series D ($ArCH=NC_6H_4X$; Ar=2-naphthyl)

Compound No.	Substituent X	m.pt. °C	Lit. m.pt. °C (ref)	Composition Atom: Found (Calculated)	Recrystallised from	Description of product
1	H	115.5	115° (54)	C88.41(88.27); H5.73(5.68); N5.92(6.06).	(1)95% ethanol (2)C_6H_6/pet ether	Pale yellow needles
2	m-F	92		C82.02(81.90); H4.85(4.86); N5.72(5.62); F7.44(7.62).	(1)95% ethanol (2)C_6H_6/pet ether	Pale yellow powder
3	p-F	134		C82.04(81.90); H4.84(4.86); N5.67(5.62); F7.45(7.62).	(1)95% ethanol (2)C_6H_6/pet ether	Pale yellow needles
4	m-Cl	109.5-110		C76.68(76.84); H4.63(4.56); N5.15(5.27); Cl13.09(13.34).	(1)95% ethanol (2)C_6H_6/pet ether	Very pale yellow needles
5	p-Cl	150		C77.04(76.84); H4.70(4.56); N5.44(5.27); Cl13.16(13.34).	(1)95% ethanol (2)C_6H_6/pet ether	Pale yellow plates
6	m-Br	112.5-113		C65.98(65.82); H4.06(3.91); N4.38(4.52); Br26.03(25.76).	(1)95% ethanol (2)C_6H_6/pet ether	Pale yellow needles
7	p-Br	147.5		C65.94(65.82); H4.05(3.91); N4.55(4.52); Br25.88(25.76).	(1)95% ethanol (2)C_6H_6/pet ether	Yellow plates
8	m-I	131.5-132		C57.32(57.16); H3.51(3.39); N3.97(3.92); I35.66(35.53).	(1)95% ethanol (2)C_6H_6/pet ether	Pale yellow needles
9	p-I	162		C57.30(57.16); H3.42(3.39); N4.06(3.92), I35.68(35.53).	(1)95% ethanol (2)C_6H_6/pet ether	Green-yellow needles
10	m-CH_3	96-96.5		C88.04(88.13); H6.29(6.16); N5.88(5.71).	(1)95% ethanol (2)C_6H_6/pet ether	Creamy-yellow plates

Table IV (Continued)

Compound No.	Substituent X	m.pt. °C	Lit. m.pt. °C (ref)	Composition Atom: Found (Calculated)	Recrystallised from	Description of product
11	p-CH_3	119-119.5		C88.13(88.13); H6.29(6.16); N5.85(5.71).	(1)95% ethanol (2)C_6H_6/pet ether	Cream-yellow needles
12	m-C_2H_5	73		C88.16(88.00); H6.66(6.60); N5.54(5.40).	95% ethanol	Pale yellow plates
13	p-C_2H_5	107		C88.40(88.00); H6.76(6.60); N5.44(5.40).	95% ethanol	Pale yellow needles
14	m-OCH_3	70-71		C82.67(82.75); H5.81(5.79); N5.55(5.36).	pet ether	Pale yellow powder
15	p-OCH_3	121.5-122		C82.79(82.75); H5.78(5.79); N5.50(5.36).	95% ethanol	Pale yellow plates
16	m-NO_2	144-144.5		C74.03(73.90); H4.48(4.38); N10.06(10.14).	(1)95% ethanol (2)C_6H_6/pet ether	Creamy powder
17	p-NO_2	185.5-186		C73.77(73.90); H4.45(4.38); N10.08(10.14).	(1)95% ethanol (2)C_6H_6	Yellow powder
18**	m-CN	113		C84.30(84.47); H4.84(4.69) N10.75(10.90).	C_6H_6	Pale cream needles
19**	p-CN	118-119		C84.31(84.47); H4.83(4.69); N10.83(10.90).	C_6H_6	Pale yellow - tan powder

Note. All compounds were prepared in 95% ethanol except those marked **, which were prepared in benzene.

Table V

Physical Data of Schiff Bases in Series E ($ArCH_6H_4X$; Ar=9-phenanthryl)

Compound No.	Substituent X	m.pt. °C	Lit. m.pt. °C (ref)	Composition Atom: Found (Calculated)	Recrystallised from	Description of product
1	H	124	120-123 (54)	C89.45(89.64); H5.55(5.38); N5.14(4.98).	95% ethanol	Pale yellow needles
2	m-F	154.5-155		C84.14(84.25); H4.88(4.72); N4.58(4.68); F6.14(6.35).	95% ethanol	Pale yellow needles
3	p-F	121.5-122.5		C84.29(84.25); H4.61(4.72); N4.68(4.68); F6.18(6.35).	95% ethanol	Pale yellow needles
4	m-Cl	123.5		C79.73(79.86); H4.66(4.48); N4.58(4.44); Cl11.22(11.23).	95% ethanol	Pale yellow needles
5	p-Cl	142.5-143		C80.13(79.86); H4.66(4.48); N4.56(4.44); Cl11.09(11.23).	95% ethanol	Pale yellow needles
6	m-Br	120-120.5		C70.02(70.01); H4.10(3.92); N3.96(3.89); Br22.27(22.18).	95% ethanol	Pale yellow needles
7	p-Br	152.5-153		C70.14(70.01); H4.02(3.92); N3.87(3.89); Br22.17(22.18).	95% ethanol	Pale yellow needles
8	m-I	135.5		C62.03(61.93); H3.60(3.47); N3.28(3.44); I31.30(31.16).	95% ethanol	Pale yellow needles
9	p-I	166.5-167		C61.79(61.93); H3.70(3.47); N3.59(3.44); I31.33(31.16).	95% ethanol	Pale yellow needles
10	m-CH_3	81-81.5		C89.43(89.45); H5.65(5.80); N4.61(4.74).	95% ethanol	Pale yellow needles

Table V (Continued)

Compound No.	Substituent X	m.pt. °C	Lit. m.pt. °C(ref)	Composition Atom: Found(Calculated)	Recrystallised from	Description of product
11	p-CH_3	113.5-114		C89.35(89.45); H5.85(5.80); N4.59(4.74).	95% ethanol	Pale yellow needles
12	m-C_2H_5	79-79.5		C89.08(89.28); H6.30(6.19); N4.35(4.53).	(1)95% ethanol (2)C_6H_6/pet ether	Yellow needles
13	p-C_2H_5	108-109		C89.16(89.28); H6.25(6.19); N4.36(4.53).	95% ethanol	Pale yellow needles
14	m-OCH_3	101.5-102		C84.72(84.86); H5.56(5.50); N4.44(4.50).	95% ethanol	Small yellow needles
15	p-OCH_3	109-110		C84.70(84.86); H5.51(5.50); N4.32(4.50).	95% ethanol	Yellow needles
16	m-NO_2	154-154.5		C77.16(77.29); H4.20(4.32); N8.49(8.58).	C_6H_6/pet ether	Small yellow needles
17**	p-NO_2	213		C77.15(77.29); H4.45(4.32); N8.70 (8.58).	C_6H_6/pet ether	Yellow needles
18**	m-CN	162.5-163		C86.11(86.27); H4.49(4.58); N9.18(9.51).	C_6H_6/pet ether	Pale yellow needles
19**	p-CN	190-191		C86.41(86.27); H4.54(4.58); N9.23(9.51).	C_6H_6	Yellow needles

Note. All compounds were prepared in 95% ethanol except those marked **, which were prepared in benzene.

Table VI

Physical Data of Schiff Bases in Series F ($ArCH{=}NC_6H_4X$; Ar=9-anthryl)

Compound No.	Substituent X	m.pt. °C	Lit. m.pt. °C (ref)	Composition Atom: Found (Calculated)	Recrystallised from	Description of product
1	H	115.5-116	108-110° (54)	C89.48(89.64); H5.49(5.38); N5.01(4.98).	95% ethanol	Deep yellow needles
2	m-F	105-106		C84.41(84.25); H4.88(4.72); N4.67(4.68); F6.51(6.35).	95% ethanol	Deep yellow needles
3	p-F	175-176		C84.10(84.25); H4.65(4.72); N4.83(4.68); F6.26(6.35).	95% ethanol	Deep yellow needles
4	m-Cl	124.5-125		C79.97(79.86); H4.55(4.48); N4.42(4.44); Cl11.32(11.23).	(1)95% ethanol (2)C_6H_6/pet ether	Deep yellow needles
5	p-Cl	154.5		C79.71(79.86); H4.45(4.48); N4.39(4.44); Cl11.32(11.23).	95% ethanol	Deep yellow needles
6	m-Br	122-122.5		C70.07(70.01); H3.83(3.92); N4.05(3.89); Br22.04(22.18).	95% ethanol	Deep yellow needles
7	p-Br	158-158.5		C70.17(70.01) H3.99(3.92); N3.76(3.89); Br22.24(22.18);	95% ethanol	Deep yellow needles
8	m-I	143.5-144		C61.94(61.93) H3.65(3.47); N3.41(3.44); I31.25(31.16).	(1)95% ethanol (2)C_6H_6/pet ether	Deep yellow needles
9	p-I	157		C62.10(61.93); H3.62(3.47); N3.47(3.44); I31.05(31.16).	95% ethanol	Deep yellow needles
10	m-CH_3	94-94.5		C89.34(89.45); H5.80(5.80); N4.57(4.74).	95% ethanol	Yellow needles

Table VI (Continued)

Compound No.	Substituent X	m.pt. °C	Lit. m.pt. °C (ref)	Composition Atom: Found (Calculated)	Recrystallised from	Description of product
11	p-CH_3	101.5-102		C89.32(89.45); H5.38(5.80); N4.84(4.74)	95 % ethanol	Orange plates
12	m-C_2H_5	90.5-91		C89.23(89.28); H6.00(6.18); N4.39(4.53).	95% ethanol	Yellow needles
13	p-C_2H_5	81		C89.11(89.28); H6.09(6.18); N4.52(4.63).	95% ethanol	Long yellow plates
14	m-OCH_3	112-112.5		C84.48(84.86); H5.59(5.50); N4.34(4.50).	95% ethanol	Long orange-yellow plates
15	p-OCH_3	152-152.5		C84.69(84.86); H5.55(5.50) N4.44(4.50).	95% ethanol	Orange plates
16	m-NO_2	186.5-187		C77.27(77.29); H4.59(4.32); N8.41(8.58).	95% ethanol	Deep yellow needles
17**	p-NO_2	191.5-192		C77.19(77.29); H4.39(4.32) N8.73(8.58)	C_6H_6/pet ether	Orange plates
18**	m-CN	155-155.5		C86.10(86.27); H4.47(4.58); N9.22(9.51).	C_6H_6/pet ether	Bright yellow needle
19**	p-CN	187-188		C86.35(86.27); H4.55(4.58); N9.16(9.51)	C_6H_6	Orange-Yellow needles

Note. All compounds were prepared in 95% ethanol except those marked **, which were prepared in benzene.

Table VII — Spectroscopic Data of Schiff Bases in Series A ($ArN=CHC_6H_4X$; $Ar=C_6H_5$)

Compound No.	Substituent X	λ max. cm^{-1} / E max.$\times 10^{-2}$			
1	H	32,400	38,050	42,250	45,800
		87	163	92	139
2	m-F	32,300(s)	38,400	42,200	45,200(s)
		89	155	99	127
3	p-F	32,500(s)	38,000	42,700(s)	44,800(s)
		86	181	86	112
4	m-Cl	33,000(s)	38,250	42,500(s)	45,800(s)
		81	142	115	193
5	p-Cl	32,000(s)	37,250	42,200(s)	44,300(s)
		102	191	78	114
6	m-Br	32,750	38,000	42,500(s)	45,400
		81	143	127	202
7	p-Br	32,200	36,850	44,000(s)	46,000(s)
		111	209	119	145
8	m-I	32,100	37,800	42,100(s)	43,750
		88	150	194	242
9	p-I	31,800(s)	35,700		44,600(s)
		126	198		139
10	m-CH_3	33,000(s)	37,750	42,500(s)	45,800(s)
		92	155	87	168

Table VII (Continued)

Compound No.	Substituent X	λ max. cm^{-1} / E max.$x10^{-2}$			
11	p-CH_3	32,500(s) 104	37,250 174	42,500(s) 79	45,600(s) 147
12	m-C_2H_5	NOT PREPARED			
13	p-C_2H_5	32,650(s) 108	37,250 178	42,500(s) 79	45,700(s) 152
14	m-OCH_3	31,700 100	37,250 138	42,500(s) 118	45,150 199
15	p-OCH_3	32,150 177	34,550 187		44,800 163
16	m-NO_2	32,500 72	38,600 204	42,300 179	
17	p-NO_2	29,500 108	34,700 138		
18	m-CN	31,550 73	39,000 136		45,100 237
19	p-CN	31,200 94	37,000 200	41,100 124	

Table VIII Spectroscopic Data of Schiff Bases in Series B ($ArCH{=}NC_6H_4X$; $Ar{=}C_6H_5$)

Compound No.	Substituent X	λ max. cm^{-1} / E max.$\times 10^{-2}$			
1	H	32,400 87	38,050 163	42,250 92	45,800 139
2	m-F	32,500(s) 55		40,300 138	45,500 100
3	p-F	32,200 93	37,800 156		45,900 139
4	m-Cl	32,500(s) 80	37,900 154	41,500(s) 102	
5	p-Cl	31,850 104	37,800 170		45,000 134
6	m-Br	32,500(s) 84	37,900 165	40,700(s) 135	
7	p-Br	31,750 112	37,750 175		45,200 137
8	m-I	32,500(s) 83	37,900(s) 174	39,700 182	
9	p-I	31,400 107	39,250 193		
10	m-CH_3	32,200 75	39,550 156	40,800(s) 152	44,700 122

Table VIII (Continued)

Compound No.	Substituent X	λ max. cm^{-1} / E max. x 10^{-2}				
11	p-CH_3	31,500 87	38,950 136	41,300 131	42,800 123	44,250 122
12	m-C_2H_5	32,000(s) 42		41,250 150		
13	p-C_2H_5	35,400 36		41,300 194		
14	m-OCH_3					
15	p-OCH_3	30,200 127	37,750 127	42,200 132	43,500 132	
16	m-NO_2	32,000(s) 93	37,350 249			45,300 215
17	p-NO_2	NOT PREPARED				
18	m-CN	31,500(s) 82	37,700 187	41,400 148		42,400 150
19	p-CN	32,000(s) 134	37,050 212			42,850 95

Table IX Spectroscopic Data of Schiff Bases in Series C ($ArN{=}CHC_6H_4X$; Ar=2-naphthyl)

Compound No.	Substituent X	λ max. cm^{-1} / E max.$\times 10^{-2}$				
1	H	31,100 84	36,000(s) 179	37,400 216	42,500 313	44,700 336
2	m-F	30,900 100	35,800(s) 174	38,200 231		44,900 353
3	p-F	31,100 115	35,700(s) 189	37,500 259		44,900 361
4	m-Cl	30,700 95	35,700(s) 164	37,800 220	42,500(s) 289	44,700 388
5	p-Cl	30,800 131	35,500(s) 245	37,000 306		44,600 371
6	m-Br	30,800 107		37,700 246		44,600 423
7	p-Br	30,700 120	35,500(s) 248	36,800 299		44,400 363
8	m-I	30,800 113	35,700(s) 204	37,400 215		44,300 397
9	p-I	30,600 139	35,300 284	36,300 295		44,000 384
10	m-CH_3	30,900 96	35,700(s) 183	37,200 226		44,400 378

Table IX (Continued)

Compound No.	Substituent X	λ max. cm^{-1} / E max.x10^{-2}				
11	p-CH_3	30,900 122	35,700(s) 233	37,000 272		44,500 370
12	m-C_2H_5	NOT PREPARED				
13	p-C_2H_5	30,800 103	35,700(s) 214	37,000 250		44,300 363
14	m-OCH_3	31,100 112	35,800(s) 160	37,300 213		44,400 393
15	p-OCH_3	30,500 166	35,400 256	36,100 247		44,300 377
16	m-NO_2	30,900 95		38,700 312	41,700 330	45,400 348
17	p-NO_2	28,000 109	34,300(s) 188	35,900 223	38,800 203	45,700 345
18	m-CN	30,700 92		38,500 229	41,500(s) 292	44,300 431
19	p-CN	30,200 98		36,800 260		44,400 325

Table X Spectroscopic Data of Schiff Bases in Series D ($ArCH=NC_6H_6X$; Ar=2-naphthyl)

Compound No.	Substituent X	λ max. cm^{-1} / E max. $\times 10^{-2}$						
1	H	31,500(s)	33,800	35,100	38,900		41,600(s)	
		122	138	135	256		199	
2	m-F	31,500(s)	33,700	34,950	38,750		41,550(s)	
		168	191	176	341		243	
3	p-F	31,550	33,850	35,050	38,850		41,550(s)	43,350(s)
		157	171	167	305		242	217
4	m-Cl	31,500(s)	33,700	34,950	38,700			
		155	181	165	321			
5	p-Cl	31,100	33,750	35,050	39,200		41,300(s)	44,750
		167	174	172	308		257	203
6	m-Br	31,500(s)	33,650	34,800	38,650		39,900(s)	
		151	180	164	315		303	
7	p-Br	31,100	33,850	35,100	38,300	40,050	41,300(s)	44,550
		151	176	176	284	367	322	219
8	m-I	31,500(s)	33,700	34,900	38,700(s)		39,900	
		175	192	180	748		374	
9	p-I	30,500	33,850	35,100	38,100(s)	40,000	41,300(s)	44,600
		154	171	175	289	383	322	215
10	m-CH_3	30,700	34,150	35,250		40,200	41,300(s)	44,500
		810	139	146		420	370	216

Table X (Continued)

Compound No.	Substituent X	λ max cm^{-1} / E max. $\times 10^{-2}$						
11	p-CH_3	30,300 129	34,100 151	35,200 157		40,150(s) 355	41,100(s) 329	
12	m-C_2H_5	31,300 139	33,900 164	35,100 164	38,500(s) 305	40,150 345		
13	p-C_2H_5	30,400 150	33,900 159	35,150 164	38,200(s) 258	40,100 328	41,000(s) 314	
14	m-OCH_3	31,000 115	33,950 156	35,100 159		39,950 373		44,800 242
15	p-OCH_3	29,300 180	33,900 155	35,100 166		40,250 320	41,000(s) 312	
16	m-NO_2			35,550 195		38,400 363	39,800(s) 342	45,500 289
17	p-NO_2	28,750 204		34,800 128			39,800(s) 221	44,600 366
18	m-CN	31,000 70	34,300 123	35,500 118		40,400 438	41,500 382	45,500 372
19	p-CN	30,700 48	34,400(s) 218	36,000 273		40,300 351	41,500(s) 284	45,250 285

Table XI Spectroscopic Data of Compounds in Series E ($ArCH=NC_6H_4X$; Ar=9-phenanthryl)

Compound No.	Substituent X	λ max. cm^{-1} / E max.$x10^{-2}$		
1	H	30,900 156	38,100(s) 350	39,850 422
2	m-F	30,600 157	38,300(s) 363	39,800 450
3	p-F	30,300 197	38,300(s) 368	39,800 409
4	m-Cl	30,500 156	38,000(s) 346	39,850 455
5	p-Cl	30,100 186	38,000(s) 372	39,800 460
6	m-Br	30,600 150	38,000(s) 343	39,850 458
7	p-Br	29,950 187	38,300(s) 384	39,700 439
8	m-I	30,200 184	37,700(s) 367	39,800 465
9	p-I	29,800 198	37,600(s) 370	39,650 462
10	m-CH_3	30,550 172	38,600(s) 379	39,800 429

Table XI (Continued)

Compound No.	Substituent X	λ max. cm^{-1} E max.$x10^{-2}$				
11	p-CH_3	30,100 178		38,500(s) 368	39,700 411	
12	m-C_2H_5	30,700 168		38,500(s) 373	39,850 436	
13	p-C_2H_5	30,100 179		38,500(s) 381	39,750 421	
14	m-OCH_3	30,650 169		38,500(s) 394	39,750 456	
15	p-OCH_3	28,800 168	30,300(s) 158	38,500(s) 357	39,700 397	
16	m-NO_2	30,200 180		38,200(s) 437	39,800 487	
17	p-NO_2	27,450 215	33,700 119	39,450 541	40,450 494	44,950 254
18	m-CN	31,300 115		40,000 405		45,400 314
19	p-CN	31,000(s) 103	33,800(s) 232	37,900 396	39,600 474	43,500(s) 263

Table XII. Spectroscopic Data of Compounds in Series F ($ArCH=NC_6H_4X$; Ar=9-anthryl)

Compound No.	Substituent X	λ max. cm^{-1} / E max.x10^{-2}			
1	H	25,250	38,900	41,100(s)	45,400
		106	798	450	246
2	m-F	24,900	38,750	41,000(s)	45,450
		100	718	472	245
3	p-F	25,250	38,850	41,100(s)	43,350
		103	779	537	246
4	m-Cl	24,900	38,700	40,800(s)	
		108	722	501	
5	p-Cl	24,800	38,700	40,700(s)	44,900
		120	761	530	289
6	m-Br	24,750	38,650	40,600(s)	
		111	734	523	
7	p-Br	24,800	38,750	40,600(s)	44,950
		115	749	518	283
8	m-I	24,750	38,700	40,700(s)	45,700
		112	725	534	369
9	p-I	24,750	38,700	40,500(s)	44,800
		130	767	557	303
10	m-CH_3	25,200	38,850	41,300(s)	
		104	822	463	

Table XII (Continued)

Compound No.	Substituent X	λ max. cm^{-1} / E max.x10^{-2}			
11	p-CH_3	25,300 111	38,900 813		44,950 274
12	m-C_2H_5	25,250 105	38,800 816		46,500 321
13	p-C_2H_5	25,200 112	38,900 807		44,950 287
14 n	m-OCH_3	25,150 109	38,800 784		
15	p-OCH_3	25,600 107	39,900 946		43,700 291
16	m-NO_2	24,650 114	38,700 728	40,900(s) 565	45,700 288
17	p-NO_2	25,400 151	39,150 786	39,800(s) 754	44,950 215
18	m-CN	24,700 113	38,900 646		41,200 525
19	p-CN	24,500 121	39,000 727		41,000 606

4.2 Polarography

4.21 Selection of the reference electrode

A mercury pool has been widely used as a reference electrode in polarographic studies in organic solvents. However, it has been suggested that this technique be used with caution and only after careful consideration, because the potential of the pool has been found to vary by as much as tens of millivolts during the recording of a polarographic wave.[56] However, the mercury pool has been shown to be a reliable reference in dimethylformamide, with tetraalkylammonium salts as backing electrolytes. In a study of the polarographic behaviour of carbonyl compounds in dimethylformamide, with tetraethylammonium iodide as supporting electrolyte, Given et al.[60] monitored the mercury pool against a saturated calomel electrode and showed that the mercury pool provided a constant and reproducible reference. The satisfactory behaviour of the pool was accounted for by assuming that mercury (II) complexes which formed maintained a high concentration of mercury (II) ions, so that further amounts of mercury (II) ions produced during the polarographic reductions had an insignificant effect upon their overall concentration.[61] In another study, measurement of the half-wave potentials of some Schiff bases in dimethylformamide, using a mercury pool as the reference and with tetrabutylammonium iodide as supporting electrolyte, were found to be reproducible to .01 volts.[57] A least squares correlation between the values obtained in this study and the half-wave potentials of the same compounds measured against an aqueous calomel reference [54] resulted in the relationship:[57]

$E_{\frac{1}{2}}$ (mercury pool) = 0.903 ± .01 $E_{\frac{1}{2}}$ (calomel) -0.468 ± .006 [31]

This excellent correlation confirms Given's conclusion with respect to the satisfactory behaviour of the mercury pool as a reference electrode in dimethylformamide.

Silver-silver ion reference electrodes have also been used successfully in solubility and complex formation studies in organic solvents,[63-68] in cells in which liquid junction potentials were reduced to a minimum. This was achieved by using a large excess of an inert electrolyte throughout the cell to provide constant ionic strength. Two further satisfactory reference systems have been described for use in dimethylformamide: (i) the $Na(Hg)|NaClO_4(s)$ couple[69] and (ii) the $Cd(Hg)|CdCl_2(s)$ couple.[62,70] The former, with sodium perchlorate as supporting electrolyte, is reported to give a stable potential over a period of months and to have a temperature coefficient of 2.3 mV/ degree. The latter has been shown to be reversible and reproducible with a number of electrolytes.

Of the above systems the mercury pool was selected as the reference electrode for this project because it has been shown to be satisfactory in dimethylformamide and is much more convenient.

4.22 Selection of the backing electrolyte

Tetraalkylammonium salts are frequently used as backing electrolytes in organic solvents because they are sufficiently soluble in these solvents. However, they are reported to undergo a rapid Hofmann elimination in dimethylformamide:[52]

$$(CH_3CH_2)_4N^+ \longrightarrow (CH_3CH_2)_3N + CH_2 = CH_2 + H^+ \qquad [32]$$

and thus act as proton donors. This evidence appears to be contradicted in a study of the influence of added proton donor (phenol) on half-wave potentials measured in dimethylformamide, with tetrabutylammonium perchlorate as backing electrolyte. The sensitivity of the half-wave potentials to added phenol was shown to be greatest in the low concentration range of added phenol.[51] This would not be so if the electrolyte itself were donating protons, since the depolariser would already be swamped with protons before the addition of phenol. Under these conditions, the addition of small amounts of proton donor would have a negligible effect upon the half-wave potential. Furthermore the electro-reduction of aromatic Schiff bases results in two well-defined waves,[54] similar to those obtained for aromatic hydrocarbons,[27] and corresponding to the suceessive addition of two single electrons to the system (Chapter 3.3). Protonation does not appear to be rapid in these molecules and the use of tetraalkylammonium salts seems to be satisfactory. Consequently, tetrabutylammonium iodide was selected as the backing electrolyte for this project.

4.3 Purification of Materials

(i) Dimethylformamide[58]

The Baker-Analysed Reagent was first dried over two successive batches of freshly dried molecular sieves, then passed down a 30-inch column of molecular sieves into a distillation flask, fitted with a nitrogen bleed. The solvent was then distilled under reduced pressure over a 24-inch refluxing column of glass helices and the centre cut (1000 ml.) of each batch (1.5 litres) retained. This was transferred, while still under partial vacuum, to a dry box filled with desiccated oxygen-free nitrogen which housed the polarograph (see Plate 1).

(ii) Tetrabutylammonium iodide

Commercial tetrabutylammonium iodide was recrystallised several times from ethyl acetate, until the product was colorless.

(iii) Nitrogen

High grade nitrogen was passed over reduced Catalyst BTS*, heated to 137° by means of an n-pentanol vapor jacket, to remove traces of oxygen. The gas was then thoroughly dried by passing it through three portions (250 ml.) of concentrated sulfuric acid, then over anhydrous calcium sulfate (Drierite) and finally over molecular sieves.

The apparatus used for purifying the nitrogen and for the distillation of the dimethylformamide is shown in Plate 2.

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*Produced by Badische Anilin-4-Soda Fabrik A.G., Ludwigshafen am Rhein (BASF Catalyst R3-11).

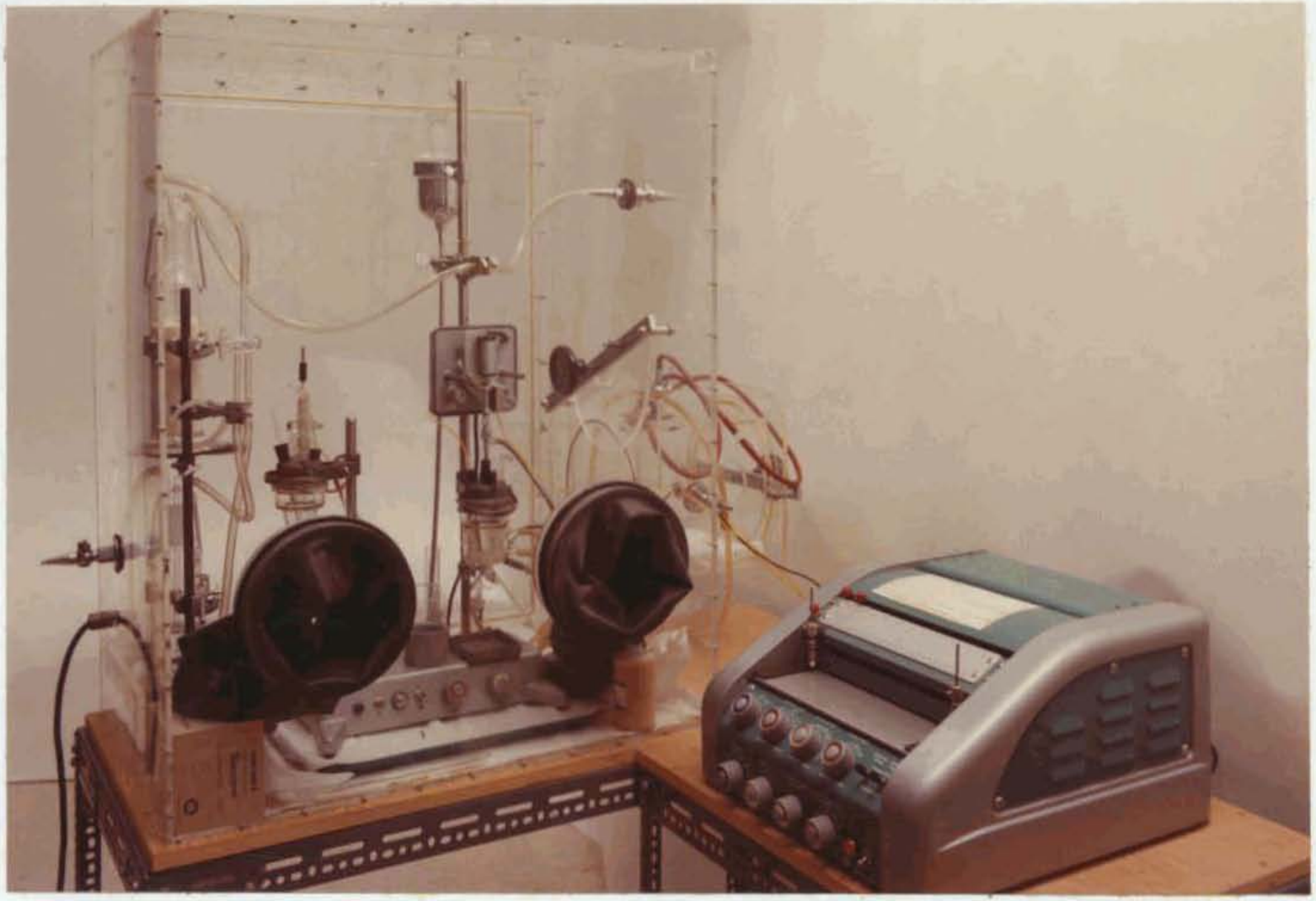


Plate 1 The Metrohm Polarecord E215R and the oxygen-free dry box containing the dropping mercury electrode.

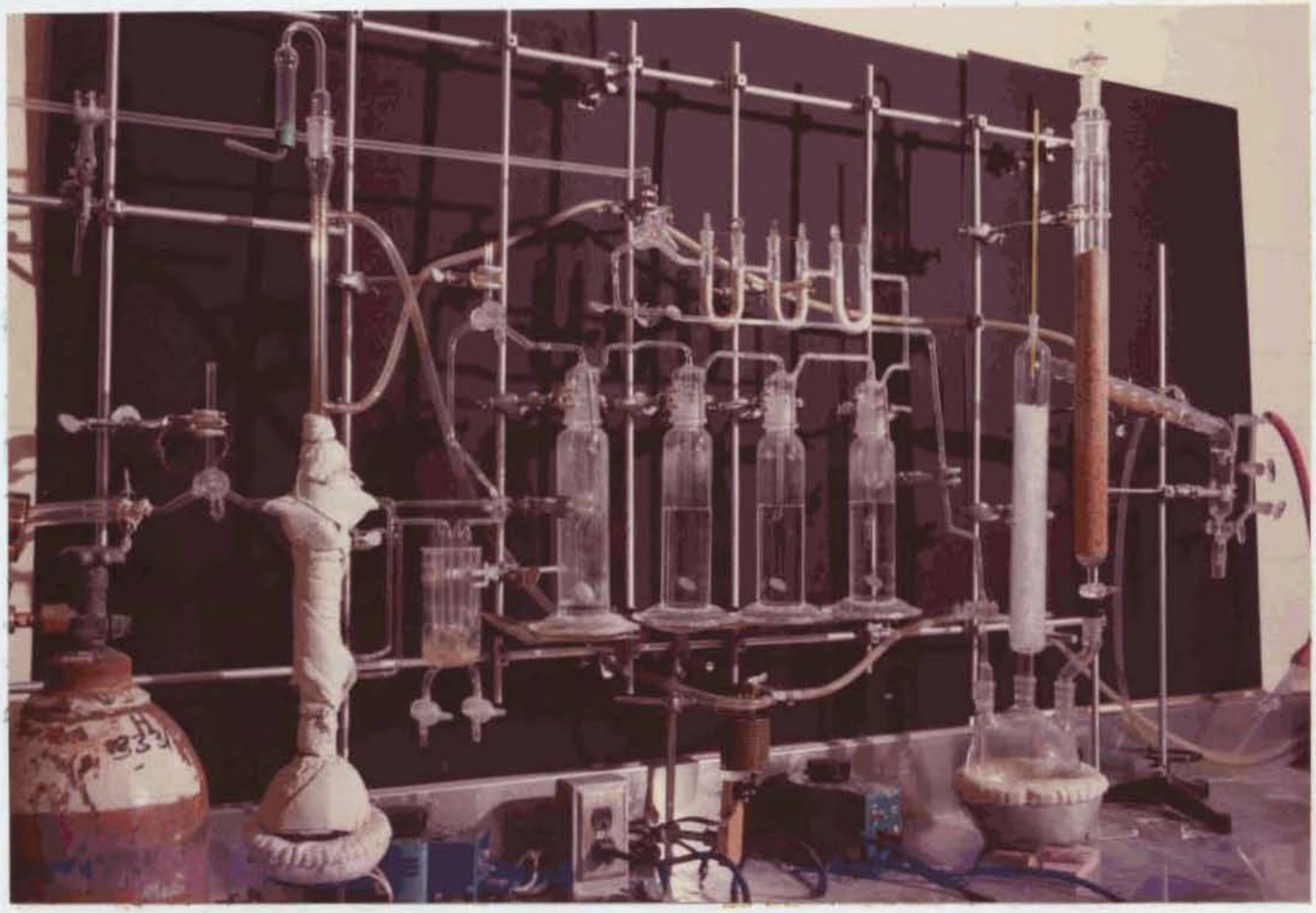


Plate 2 Apparatus for purifying the nitrogen and for distilling the dimethylformamide.

4.4 Experimental Procedure

Polarograms of all compounds were obtained by means of a Beckman Electroscan TM30. Some polarograms were also obtained using a Metrohm Polarecord E215R. All polarograms were obtained in dimethylformamide with tetrabutylammonium iodide as backing electrolyte, using 'rapid drop' polarography. In this technique the mercury drop is not allowed to form and fall naturally, but is ejected at regular intervals by an electromechanical impulse. All polarographic solutions were prepared, and all polarographic measurements made under oxygen-free nitrogen in a dry box. (Plate 1). Evacuated sample tubes containing weighed portions of tetrabutylammonium iodide (1.85 ± .05g) or the Schiff bases were transferred to the dry box. Solutions for polarography were prepared by placing the tetrabutylammonium iodide together with a suitable portion of the appropriate Schiff base and purified dimethylformamide (50 ml.) in a thermostatically controlled cell, at 25.0 ± .01°C, containing a platinum electrode immersed in a pool of mercury. A preliminary polarogram was recorded over the voltage range 0 to -2V, followed by a second polarogram, recorded over a narrower 0.5 V or 1.0 V range. The latter was used to determine the half-wave potentials. Polarograms were recorded for every compound at two drop-time settings, corresponding to 3.5 drops/second and 4.0 drops/second respectively. The average value of both half-wave potentials was used throughout the thesis.

The majority of the polarograms obtained on the Beckman Electroscan TM 30 recording system were analysed by the procedure recommended by Meites.[82] On each polarogram, a lower base line (B-B')

and an upper plateau (P-P') were constructed to represent the mean current preceeding and following the first wave. (see Fig. 4.2). On the rising part of the wave, twelve equally spaced regular oscillations were selected and the point midway between the maximum and the minimum on the rising part of each of the selected oscillations was marked. The values of i, the current, and $i_d - i$ (Fig. 4.2) were measured for each of these oscillations. A computer program was used to evaluate a plot of the applied potential, $E_{d.m.e.}$, against $\log\{i/(i_d-i)\}$ and to calculate the value of the half-wave potential. The half-wave potential was the value of $E_{d.m.e.}$ which corresponded to a value of zero for $\log\{i/(i_d-i)\}$.

For some compounds it was not possible to separate the first polarographic wave from successive waves with sufficient clarity to give reliable half-wave potentials by the above method. In such cases the half-wave potentials were obtained by means of a Metrohm recording system, which recorded the polarograms in a differentiated form. The relationship between the measurements obtained on both recording systems was established by measuring the half-wave potentials of a number of compounds on both instruments and correlating the two sets of values thus obtained.

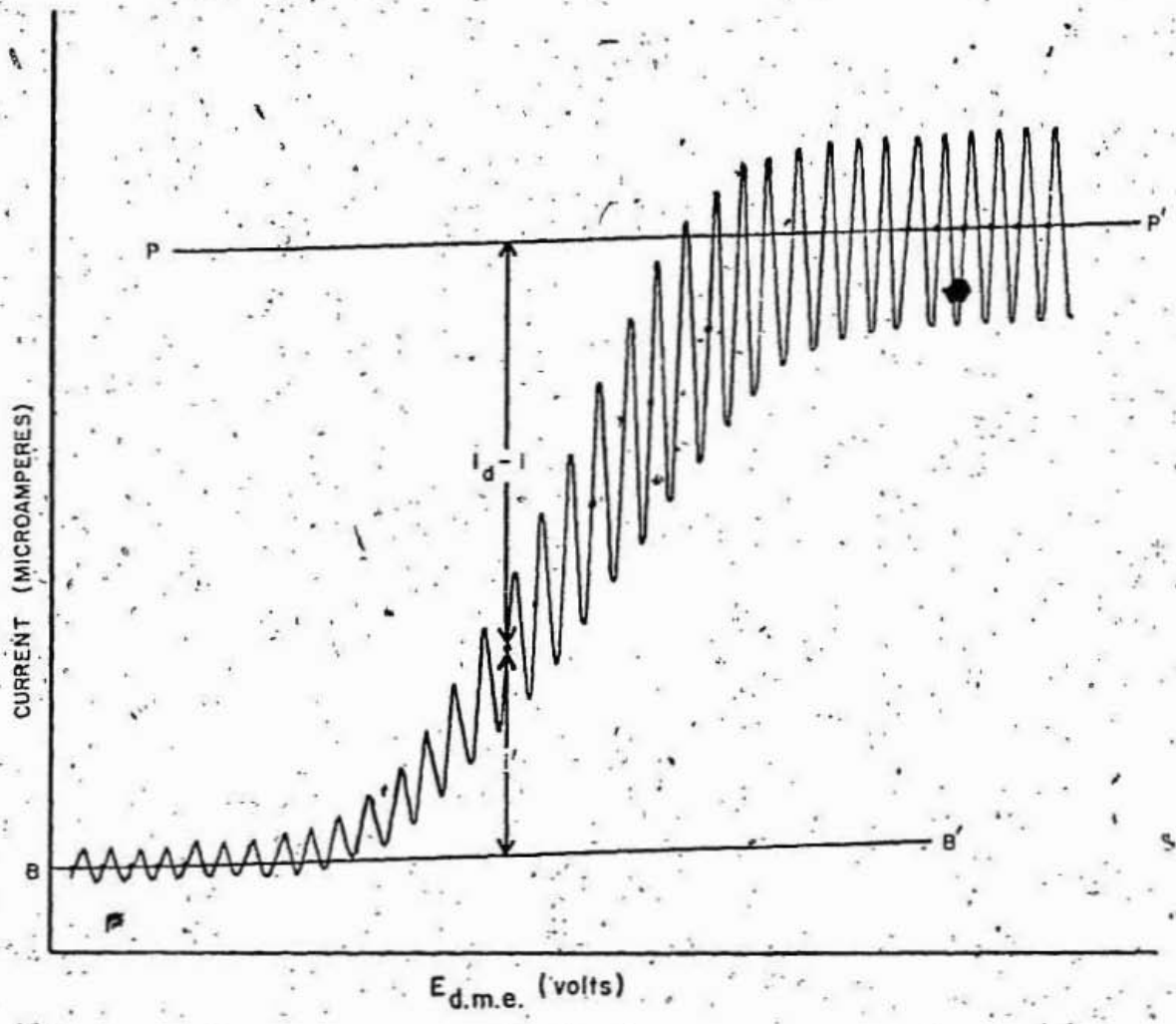


Fig. 4.2 Diagram of a typical polarogram

CHAPTER 5

RESULTS AND DISCUSSION OF POLAROGRAPHIC DATA

5.1 Introduction

Most $E_{\frac{1}{2}}$ - M.O. correlations in the literature[23,53] have used polarographic data measured in solvents containing proton donors (water, alcohols) or in non-aqueous solvents of doubtful purity. H. B. Mark, Jr.[51] observes that the theoretical significance of the correlations obtained, especially the value of the resonance integral, β , obtained from the slope of the line, is extremely doubtful and is only valid for the hydrocarbons in the series under consideration (see Chapter 3.1). In this study, special care has been taken to reduce and standardise these effects by using only pure, dry solvents and reactants. This precautionary measure was necessitated because it has been shown that even small concentrations of proton donor cause significant errors in the measurement of half-wave potentials.[51]

The half-wave potentials obtained on the Electroscan TM30 and Metrohm Polarecord E215R recording systems were not directly comparable but a least squares analysis of the half-wave potentials of thirty-two Schiff bases, measured with both instruments, gave the following correlation:

$$E_{\frac{1}{2}}(ES) = (0.9731 \pm 0.0130)E_{\frac{1}{2}}(M) - (0.0035 \pm .0155) \qquad [33]$$

where $E_{\frac{1}{2}}(ES)$ and $E_{\frac{1}{2}}(M)$ are the respective values recorded on the Electroscan TM30 and Metrohm Polarecord E215R instruments.

In a number of cases it was not possible to determine $E_{\frac{1}{2}}(ES)$ directly by employing the method prescribed by Meites.[82] In these cases the half-wave potentials recorded on the Metrohm Polarecord E215R, $E_{\frac{1}{2}}(M)$, were converted to $E_{\frac{1}{2}}(ES)$ by the application of Equation [33]. Values determined by this procedure are marked with an asterisk (*) in Tables XIII to XVIII.

The half-wave potentials of the Schiff bases in Series A to F are recorded in Tables XIII to XVIII and the average values, used throughout the remainder of this thesis, are summarised in Table XIX.

The influence of substituents and of changes in the aromatic system of the molecule upon the half-wave potential have been investigated.

Table XIII Half-wave Potentials (in Volts) of Schiff Bases in Series A ($ArN{=}CHC_6H_4X$; $Ar{=}C_6H_5$)

Compound No.	Substituent X	E(ES) Drop-time 1	E(ES) Drop-time 2	E(ES) Average	E(M)
1	H	-1.3801	-1.3847	-1.3824	-1.428
2	m-F	-1.2718	-1.2808	-1.2763	-1.298
3	p-F	-1.3852	-1.3810	-1.3831	-1.415
4	m-Cl	-1.2386	-1.2321	-1.2354	-1.253
5	p-Cl			-1.2325*	-1.263
6	m-Br			-1.1537*	-1.182
7	p-Br			-1.1080*	-1.135
8	m-I	-1.0611	-1.0601	-1.0606	-1.089
9	p-I	-1.0536	-1.0549	-1.0543	-1.074
10	m-CH_3	-1.4325	-1.4382	-1.4354	-1.457
11	p-CH_3	-1.4404	-1.4407	-1.4406	-1.489
12	m-C_2H_5				
13	p-C_2H_5	-1.4113	-1.4081	-1.4097	-1.455
14	m-OCH_3	-1.3848	-1.3938	-1.3893	
15	p-OCH_3	-1.4947	-1.4948	-1.4948	-1.537
16	m-NO_2			-1.4456*	-1.482
17	p-NO_2	-0.3761	-0.3767	-0.3764	
18	m-CN	-1.1138	-1.1152	-1.1145	
19	p-CN	-0.9410	-0.9470	-0.9440	

E(ES) - Half-wave potentials determined on Electroscan

E(M) - Half-wave potentials determined on Metrohm

Drop-time 1 : ~3.5 drops/second

Drop-time 2 : ~4.0 drops/second

*E(ES) calculated from E(M)

Table XIV Half-wave Potentials (in Volts) of Schiff Bases in Series B ($ArCH{=}NC_6H_4X$; $Ar{=}C_6H_5$)

Compound No.	Substituent X	E(ES) Drop-time 1	E(ES) Drop-time 2	E(ES) Average	E(M)
1	H	-1.3801	-1.3847	-1.3824	
2	m-F	-1.2886	-1.2860	-1.2873	
3	p-F	-1.3861	-1.3885	-1.3873	
4	m-Cl	-1.2582	-1.2574	-1.2578	
5	p-Cl	-1.2744	-1.2765	-1.2755	
6	m-Br	-1.2058	-1.2052	-1.2055	-1.224
7	p-Br			-1.1741*	-1.203
8	m-I	-1.0915	-1.0970	-1.0943	-1.100
9	p-I	-1.0927	-1.0920	-1.0924	-1.120
10	m-CH_3	-1.3955	-1.3996	-1.3976	
11	p-CH_3	-1.4255	-1.4303	-1.4279	
12	m-C_2H_5	-1.3889	-1.3923	-1.3906	
13	p-C_2H_5	-1.3789	-1.3858	-1.3824	
14	m-OCH_3	-1.3862	-1.3757	-1.3720	
15	p-OCH_3	-1.4588	-1.4657	-1.4623	
16	m-NO_2			-0.5669*	-0.579
17	p-NO_2				
18	m-CN			-1.1401*	-1.168
19	p-CN	-0.9882	-0.9893	-0.9888	-1.021

E(ES) - Half-wave potentials determined on Electroscan

E(M) - Half-wave potentials determined on Metrohm

Drop-time 1 : ≃3.5 drops/second

Drop-time 2 : ~4.0 drops/second

*E(ES) calculated from E(M)

Table XV. Half-wave Potentials (in Volts) of Schiff Bases in Series C ($ArN=CHC_6H_4X$; Ar=2-napthyl)

Compound No.	Substituent X	E(ES) Drop-time 1	E(ES) Drop-time 2	E(ES) Average	E(M)
1	H	-1.2859	-1.2889	-1.2874	
2	m-F	-1.1629	-1.1666	-1.1648	
3	p-F	-1.2572	-1.2559	-1.2566	
4	m-Cl	-1.1386	-1.1428	-1.1407	
5	p-Cl			-1 1712*	-1.200
6	m-Br			-1.1128*	-1.140
7	p-Br			-1.0749*	-1.101
8	m-I			-1.0068*	-1.031
9	p-I	-0.9587	-0.9566	-0.9577	
10	m-CH_3	-1.2772	-1.2773	-1.2773	
11	p-CH_3	-1.3123	-1.3155	-1.3139	
12	m-C_2H_5				
13	p-C_2H_5	-1.3040	-1.3062	-1.3051	-1.351
14	m-OCH_3	-1.2544	-1.2539	-1.2542	
15	p-OCH_3	-1.3612	-1.3629	-1.3621	
16	m-NO_2			-0.5348*	-0.546
17	p-NO_2	-0.3256	-0.3290	-0.3273	
18	m-CN	-1.0210	-1.0218	-1.0214	-1.049
19	p-CN	-0.8860	-0.8855	-0.8858	-0.927

E(ES) - Half-wave potentials determined on Electroscan

E(M) - Half-wave potentials determined on Metrohm

Drop-time 1 : ~ 3.5 drops/second

Drop-time 2 : ~ 4.0 drops/second

*E(ES) calculated from E(M)

Table XVI Half-wave Potentials (in Volts) of Schiff Bases in Series D ($ArCH{=}NC_6H_4X$; Ar=2-naphthyl)

Compound No.	Substituent X	E(ES) Drop-time 1	E(ES) Drop-time 2	E(ES) Average	E(M)
1	H	-1.2755	-1.2730	-1.2743	
2	m-F	-1.1567	-1.1602	-1.1585	
3	p-F	-1.2445	-1.2498	-1.2472	
4	m-Cl	-1.1546	-1.1515	-1.1531	
5	p-Cl	-1.1721	-1.1781	-1.1751	
6	m-Br			-1.1099*	-1.137
7	p-Br			-1.1128*	-1.140
8	m-I			-1.0467*	-1.072
9	p-I			-1.0213*	-1.046
10	m-CH_3	-1.2721	-1.2735	-1.2728	
11	p-CH_3	-1.2976	-1.2994	-1.2981	
12	m-C_2H_5	-1.2948	-1.2884	-1.2916	
13	p-C_2H_5	-1.3174	-1.2975	-1.3075	
14	m-OCH_3	-1.2416	-1.2337	-1.2377	
15	p-OCH_3	-1.3469	-1.3562	-1.3516	
16	m-NO_2	-0.5948	-0.5976	-0.5962	
17	p-NO_2	-0.5593	-0.5613	-0.5603	-0.545
18	m-CN	-1.0693	-1.0681	-1.0687	-1.091
19	p-CN	-0.9423	-0.9489	-0.9456	-0.989

E(ES) - Half-wave potentials determined on Electroscan

E(M) - Half-wave potentials determined on Metrohm

Drop-time 1 : ~3.5 drops/second

Drop-time 2 : ~4.0 drops/second

*E(ES) calculated from E(M)

Table XVII Half-wave Potentials (in Volts) of Schiff Bases in Series E ($ArCh{=}NC_6H_4X$; Ar=9-phenanthryl)

Compound No.	Substituent X	E(ES) Drop-time 1	E(ES) Drop-time 2	E(ES) Average	E(M)
1	H	-1.1784	-1.1781	-1.1765	
2	m-F	-1.1010	-1.1009	-1.1010	
3	p-F	-1.1732	-1.1701	-1.1717	
4	m-Cl	-1.0893	-1.0873	-1.0883	
5	p-Cl	-1.1043	-1.1100	-1.1072	
6	m-Br	-1.0935	-1.0921	-1.0928	
7	p-Br			-1.0963*	-1.123
8	m-I			-0.9630*	-0.986
9	p-I			-0.9854*	-1.009
10	m-CH_3	-1.1945	-1.2005	-1.1975	
11	p-CH_3	-1.2102	-1.2088	-1.2095	
12	m-C_2H_5	-1.1913	-1.1997	-1.1955	
13	p-C_2H_5	-1.2095	-1.2078	-1.2087	
14	m-OCH_3	-1.1618	-1.1626	-1.1622	
15	p-OCH_3	-1.2350	-1.2403	-1.2377	
16	m-NO_2	-0.5843	-0.5850	-0.5847	
17	p-NO_2			-0.5523*	-0.564
18	m-CN	-0.9868	-0.9869	-0.9869	-1.025
19	p-CN			-0.9046*	-0.926

E(ES) - Half-wave potentials determined on Electroscan

E(M) - Half-wave potentials determined on Metrohm

Drop-time 1 : ~ 3.5 drops/second

Drop-time 2 : ~ 4.0 drops/second

*E(ES) calculated from E(M)

Table XVIII Half-wave Potentials (in Volts) of Schiff Bases in Series F ($ArCH{=}NC_6H_4X$; Ar=9-anthryl)

Compound No.	Substituent X	E(ES) Drop-time 1	E(ES) Drop-time 2	E(ES) Average	E(M)
1	H	-0.8602	-0.8568	-0.8585	
2	m-F	-0.7873	-0.7892	-0.7883	
3	p-F	-0.8577	-0.8569	-0.8573	
4	m-Cl	-0.7771	-0.7800	-0.7786	
5	p-Cl	-0.8117	-0.8112	-0.8115	
6	m-Br	-0.7764	-0.7743	-0.7754	
7	p-Br	-0.8013	-0.8029	-0.8021	
8	m-I	-0.7894	-0.7849	-0.7872	
9	p-I	-0.8058	-0.8010	-0.8034	
10	m-CH_3	-0.8769	-0.8742	-0.8756	
11	p-CH_3	-0.8882	-0.8931	-0.8907	
12	m-C_2H_5	-0.8715	-0.8749	-0.8732	
13	p-C_2H_5	-0.8884	-0.8879	-0.8882	
14	m-OCH_3	-0.8540	-0.8521	-0.8531	
15	p-OCH_3	-0.9086	-0.9107	-0.9097	
16	m-NO_2	-0.5633	-0.5619	-0.5626	
17	p-NO_2			-0.4920*	-0.502
18	m-CN	-0.7404	-0.7432	-0.7418	-0.778
19	p-CN	-0.6902	-0.6951	-0.6927	-0.706

E(ES) - Half-wave potentials determined on Electroscan

E(M) - Half-wave potentials determined on Metrohm

Drop-time 1 : ~3.5 drops/second

Drop-time 2 : ~4.0 drops/second

*E(ES) calculated from E(M).

Table XIX Summary of Polarographic Data. Average Half-ware Potentials

Compound no.	Substituent.	Series A	Series B	Series C	Series D	Series E	Series F
1	H	-1.3824	-1.3824	-1.2874	-1.2743	-1.1765	-0.8585
2	m-F	-1.2763	-1.2873	-1.1648	-1.1585	-1.1010	-0.7883
3	p-F	-1.3831	-1.3873	-1.2568	-1.2472	-1.1717	-0.8573
4	m-Cl	-1.2354	-1.2578	-1.1407	-1.1531	-1.0883	-0.7786
5	p-Cl	-1.2325	-1.2755	-1.1712	-1.1754	-1.1072	-0.8115
6	m-Br	-1.1537	-1.2055	-1.1128	-1.1099	-1.0928	-0.7754
7	p-Br	-1.1080	-1.1741	-1.0749	-1.1128	-1.0963	-0.8021
8	m-I	-1.0606	-1.0943	-1.0068	-1.0467	-0.9630	-0.7872
9	p-I	-1.0543	-1.0924	-0.9577	-1.0213	-0.9854	-0.8034
10	m-CH_3	-1.4354	-1.3976	-1.2773	-1.2728	-1.1975	-0.8756
11	p-CH_3	-1.4406	-1.4279	-1.3139	-1.2981	-1.2095	-0.8907
12	m-C_2H_5	**	-1.3906	**	-1.2916	-1.1955	-0.8732
13	p-C_2H_5	-1.4097	-1.3824	-1.3051	-1.3075	-1.2087	-0.8882
14	m-OCH_3	-1.3893	-1.3720	-1.2542	-1.2377	-1.1622	-0.8531
15	p-OCH_3	-1.4948	-1.4623	-1.3621	-1.3516	-1.2377	-0.9097
16	m-NO_2	-1.4456	-0.5669	-0.5348	-0.5962	-0.5847	-0.5626
17	p-NO_2	-0.3764	**	-0.3273	-0.5603	-0.5525	-0.4920
18	m-CN	-1.1145	-1.1401	-1.0214	-1.0687	-0.9869	-0.7418
19	p-CN	-0.9440	-0.9888	-0.8858	-0.9456	-0.9046	-0.6927

* Reduction potentials are recorded in volts.

** Compounds not prepared.

5.2 Substituent Effects

The half-wave potentials of, for example, the meta-fluoro derivative of each series of Schiff bases was plotted against the half-wave potential of the corresponding parent or unsubstituted compound. A straight line correlation was obtained. Similar plots were made for each substituent in turn giving satisfactory correlations in the majority of cases. These correlations are shown in Figures 5.1 to 5.18. Least squares correlations were determined and the results recorded in Table XX.

The behaviour of the meta- and para- nitro derivatives are clearly anomalous. The para- nitro derivatives are all reduced at similar voltages, between -0.30 volts and -0.60 volts. Similarly, with one exception, the meta- nitro derivatives are reduced at potentials ranging between -0.55 volts and -0.60 volts. (The exception is Compound 16, Series A which reduces at -1.446 volts). These results suggest that the nitro group is being reduced in preference to the π-system of the molecule. It is also evident that some compounds which, like the nitro derivatives, have substituents that are themselves reducible, give less satisfactory correlations. The meta- and para-bromo and iodo and the para- cyano derivatives illustrate this.

The slope of the line obtained for each substituent, M_S, is a characteristic of the substituent; that is, it is a substituent constant and is independent of the rest of the molecule. It might be expected, therefore, that these slopes should favourably correlate with the appropriate Hammett substituent (σ) constants. This was confirmed by plotting σ against M_S (Fig. 5.19).

Table XX Summary of Correlation Data for Substituent Plots in Figures 5.1-5.18 Hammett σ Values[1], and σ_{SB} Values[2].

Substituent	Slope (Π_S)	Intercept	Substituent Constants	σ_{SB}[2]
m-F	0.925 ± .039	.005 ± .048	.34	.095
p-F	0.992 ± .039	.000 ± .048	.06	-.005
m-Cl	0.881 ± .041	-.028 ± .051	.37	.125
p-Cl	0.840 ± .045	-.098 ± .056	.23	.107
m-Br	0.758 ± .083	-.145 ± .103	.39	.177
p-Br	0.633 ± .109	-.285 ± .135	.23	.208
m-I	0.556 ± .047	-.311 ± .058	.35	.288
p-I	0.490 ± .081	-.584 ± .101	.27	.290
m-CH_3	1.013 ± .055	.001 ± .068	-.07	-.015
p-CH_3	0.028 ± .030	-.003 ± .037	-.17	-.046
m-C_2H_5	0.933 ± .014	-.023 ± .017	-.05	-.008
p-C_2H_5	0.968 ± .028	-.062 ± .034	-.15	0.000
m-OCH_3	0.992 ± .042	.005 ± .052	.11	.010
p-OCH_3	1.084 ± .033	.027 ± .041	-.27	-.080
m-NO_2	0.710 ± .841	-.156 ± 1.04	*	.816
p-NO_2	-0.198 ± .277	-.699 ± .335	*	*
m-CN	0.727 ± .053	-.121 ± .066	.68	.242
p-CN	0.509 ± .079	-.368 ± .098	.66(1.00)[3]	.394

1. Substituent constants have been selected from Zuman[23] (Table III-1, p. 46-48)
2. σ_{SB} values are those generated from the Schiff base in Series B, by applying the equation $\sigma_{SB} = E^B_{\frac{1}{2}}(X) - E^B_{\frac{1}{2}}(H)$
3. The σ value (bracketed) has been applied to p-CN derivatives.

Good correlations were obtained except for the m-Br, p-Br, m-I, p-I, m-NO_2, p-NO_2 and p-CN derivatives which deviated from the correlation line. The slopes obtained for these substituents are not proportional to their Hammett substituent constant. It appears likely, therefore, that the mechanisms for the polarographic reduction of these compounds are different from the mechanism which applies to the majority of the Schiff bases.

Further evidence of the unusual behaviour of the above derivatives at the dropping mercury electrode was obtained by applying Equation [28] to the data obtained for the Schiff bases. The application of this equation to a wide variety of reaction series of benzene derivatives and other reaction series gave good correlations in the majority of cases. Where deviations of half-wave potentials from the straight line obtained by plotting $-E_{\frac{1}{2}}$ against σ do occur, it was generally assumed that those substances which deviate from the correlation line are reduced at the electrode by a different mechanism from that which applies to the rest of the reaction series.[23]

The correlations obtained for the Schiff bases by plotting the half-wave potentials against the corresponding Hammett substituent constants for each series of compounds are shown in Figures 5.20 to 5.25 and the least squares data is tabulated in Table XXI. (The Hammett substituent constants used in this correlation are tabulated in Table XIV).

In some reaction series the meta- and para- bromo and iodo derivatives deviate from the correlation line. This tends to confirm that the mechanism of the reduction of these compounds at the electrode

surface is not the same mechanism by which the majority of the compounds in the series are reduced.

Table XXI Data for the Correlations of the Half-wave Potentials for Compounds in Series A, B, C, D, E and F Versus the Hammett σ Values

Series	Slope (ρ)*	Intercept
A	0.418 ± .026	-1.386 ± .026
B	0.355 ± .021	-1.376 ± .008
C	0.364 ± .014	-1.268 ± .005
D	0.307 ± .009	-1.263 ± .004
E	0.263 ± .010	-1.176 ± .004
F	0.181 ± .007	-0.858 ± .003

*Values for compounds which deviated from the line were not included in the calculation of the ρ-values.

Zuman[23] reports that halogen substituents are among the most frequent deviants when the Hammett equation is applied to the polarographic reduction of benzene derivatives. Halogen atoms are said to be "deformable" and are thought to act as "electron bridges" in some electrode reactions. Thus, in Zuman's words, "it is possible that the orientation of the molecule in the transition state for the halogen derivative would differ from that of most other members in the reaction series".[23] A different mechanism would therefore apply to the reduction of the halogen derivatives.

The first step in the mechanism for the normal reduction of Schiff bases at the dropping mercury electrode is considered to be the addition of an electron to the π-system of the molecule, with the

subsequent reduction of the > C = N- bond. However, when a reducible substituent is present in the molecule, the first step in the reduction may involve either the substituent or the π-system of the molecule, depending which of the two is the more easily reduced.

In Series A, B, C and D the half-wave potentials of meta- and para- bromo and iodo derivatives fall well below the correlation line. In Series E, only the meta- and para- iodo derivatives fall below the line while in Series F, all the halogen derivatives fall on the correlation line. (Figs. 5.20 to 5.25). In those compounds which deviate from the correlation, it appears that the halogen atom is being reduced in preference to the π-system of the molecule. If Zuman[23] is correct, the bromine and iodine atoms act as "electron bridges" in the reduction of these molecules. In Series E and F, the ease of entry of an electron into the π-system of the molecule (as measured by the half-wave potential of the corresponding unsubstituted Schiff base) increases, so that in Series E (Fig. 5.24) the normal mechanism applies to the bromo derivatives and the electron enters the π-system of the molecule. In Series F (Fig. 5.25) the normal mechanism applies to all the halogen derivatives.

The half-wave potentials of the para- cyano derivatives fall below the correlation line in every series of Schiff bases if the Hammett σ value is used. However, if σ^- is used, the half-wave potentials of the para- cyano derivatives fall on the line in every case. The > C = N- group is in mesomeric interaction with the para- cyano substituent through the benzene ring and it is not uncommon, in such cases, for σ^- (derived from the reactions of para- substituted phenols

and anilines) to give a better fit than σ. However, Zuman[23] also reports that a change in mechanism occurs in some para-cyano derivatives, resulting in the reduction of the -CN group to yield $-CH_2NH_2$.

The mechanisms by which the deviating substituents were reduced have been shown to be self-consistent in the Schiff bases by adopting a standard series of Schiff bases and generating sigma values for each substituent from the half-wave potentials of the standard series. The sigma values were then correlated with the half-wave potentials of the other Schiff base series.

The series of Schiff bases derived from benzaldehyde and substituted anilines (Series B) was taken as the standard series. The sigma values (designated σ_{SB} to differentiate them from the Hammett σ constants) are defined as:

$$\sigma_{SB} = E_{\frac{1}{2}}^{B}(X) - E_{\frac{1}{2}}^{B}(H) \qquad [34]$$

where $E_{\frac{1}{2}}^{B}(X)$ and $E_{\frac{1}{2}}^{B}(H)$ are the respective half-wave potentials of the substituted and unsubstituted derivatives in Series B. The σ_{SB} values are tabulated in Table XX.

Correlations of the half-wave potentials of the compounds in Series A, C, D, E and F with σ_{SB} values are shown in Figures 5.26 to 5.30 respectively and the correlation data recorded in Table XXII.

In these correlations, the meta- and para- bromo and iodo compounds do not diverge from the correlation lines in Series A, C, D and E but, as might be expected, they yield a less satisfactory correlation in Series F. This suggests that the deviating bromo and iodo derivatives are reduced by a consistent mechanism throughout.

Similarly the meta- nitro derivatives fall on the correlation line in every case, suggesting that the reduction mechanism for these substituents, though different from that of the majority of the compounds in the series, is also consistent.

Table XXII Data from the Correlations of the Half-wave Potentials of Compounds in Series A, B, C, D, E and F versus σ_{SB}

Series	Slope, ρ_{SB}^*	Intercept
A	1.185 ± .036	-1.390 ± .006
B	1.000	
C	0.933 ± .023	-1.268 ± .006
D	0.819 ± .029	-1.271 ± .007
E	0.721 ± .024	-1.185 ± .006
F	0.373 ± .028	-0.862 ± .007

The slopes obtained in the above correlations, ρ_{SB}, are characteristic of the reaction series, i.e., they are reaction constants and should therefore be proportional to the Hammett ρ values calculated earlier (Table XXI). The correlation of these two constants is shown in Fig. 5.31. A least squares analysis of the data provided the relationship:

$$\text{(Hammett) } \rho = (0.299 \pm 0.023)\, \rho_{SB} + (0.639 \pm 0.020). \quad [35]$$

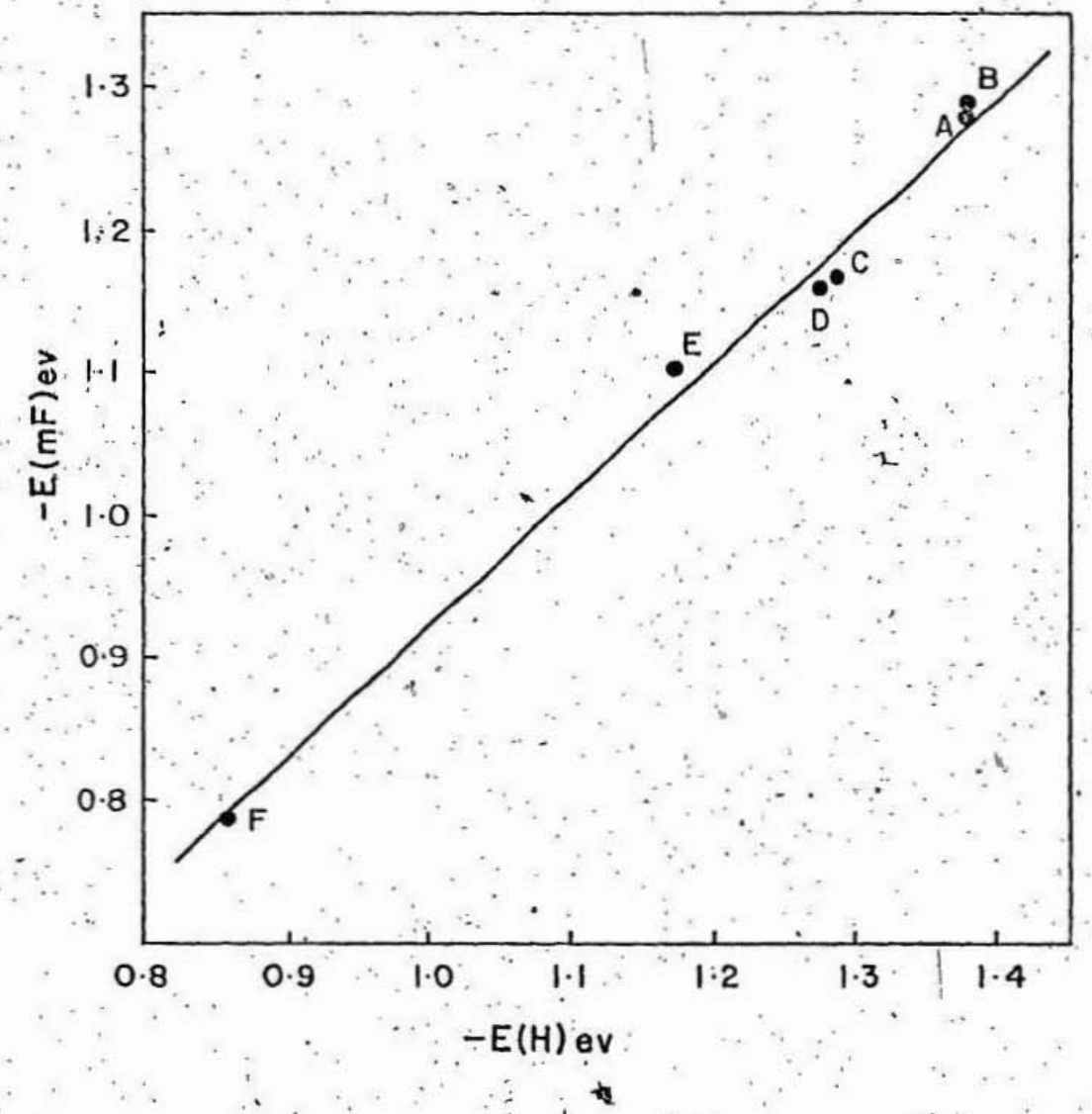


Fig. 5.1. Correlation of half-wave potentials of meta-fluoro derivatives, -E(mF), in Series A to F with those of the corresponding unsubstituted compounds, -E(H).

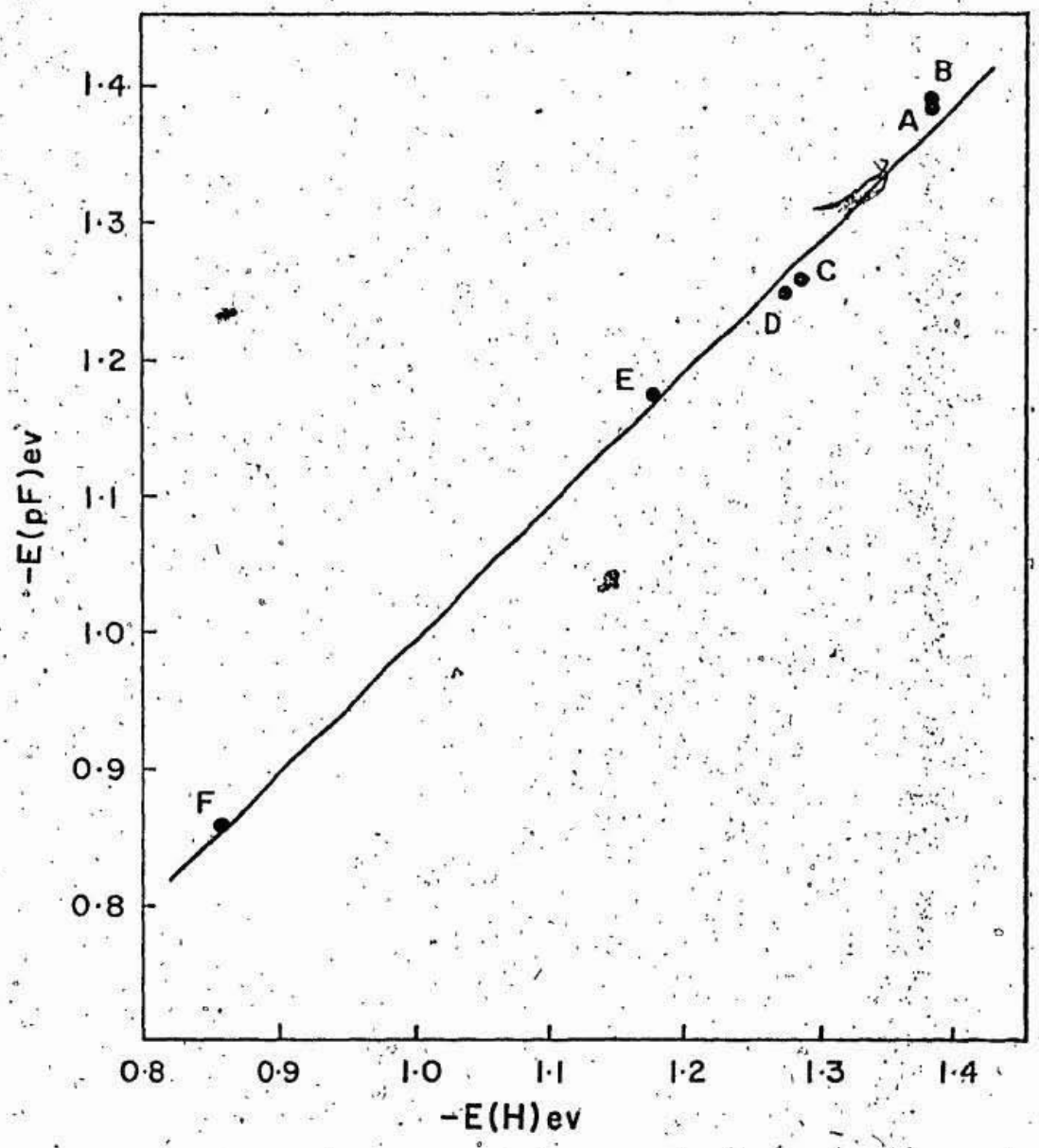


Fig. 5.2 Correlation of half-wave potentials of para-fluoro derivatives, -E(pF), in Series A to F with those of the corresponding unsubstituted compounds, -E(H).

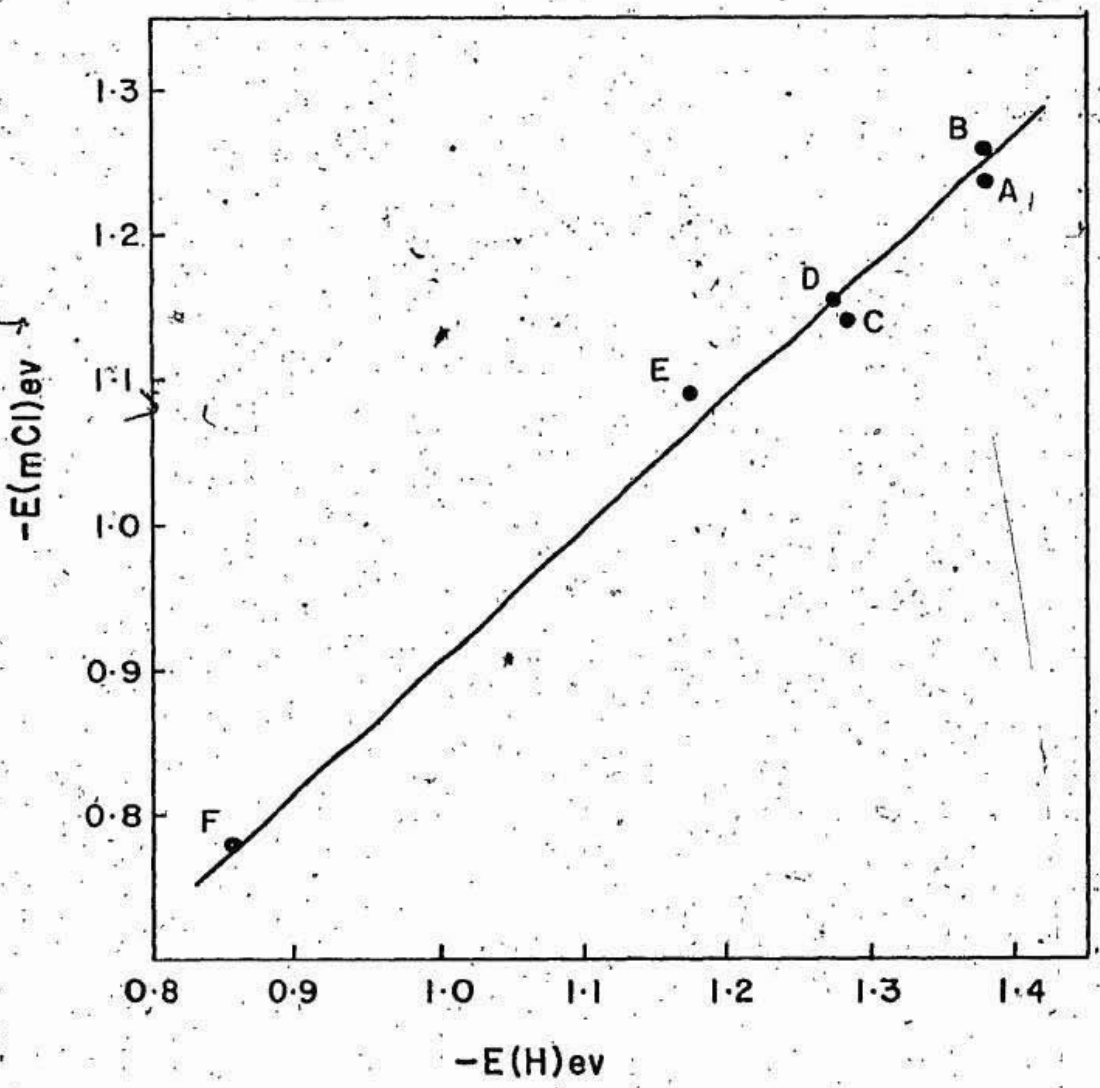


Fig. 5.3 Correlation of half-wave potentials of meta-chloro derivatives in Series A to F with those of the corresponding unsubstituted compounds.

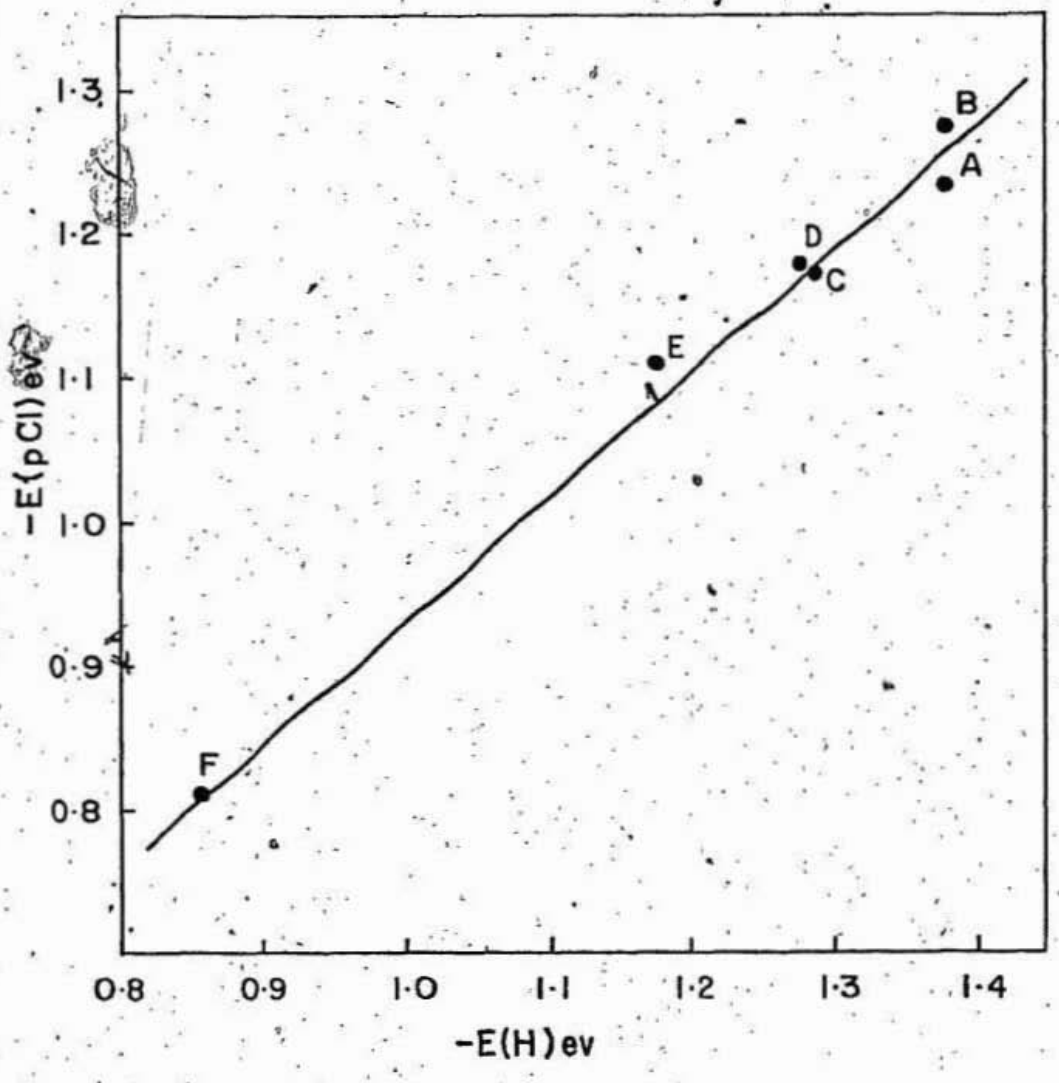


Fig. 5.4 Correlation of half-wave potentials of para-chloro derivatives in Series A to F with those of the corresponding unsubstituted compounds

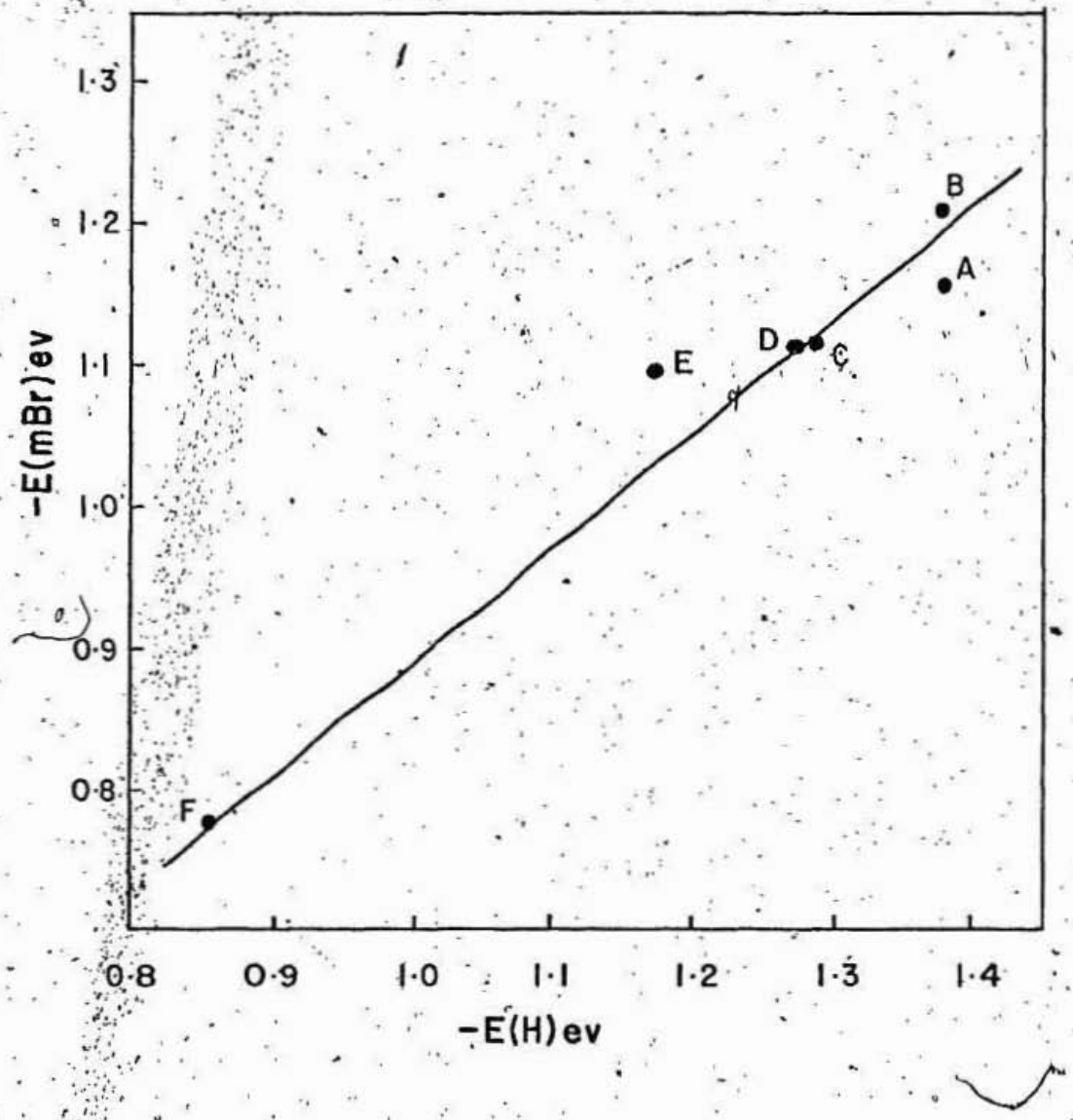


Fig. 5.5 Correlation of half-wave potentials of meta-bromo derivatives in Series A to F with those of the corresponding unsubstituted compounds.

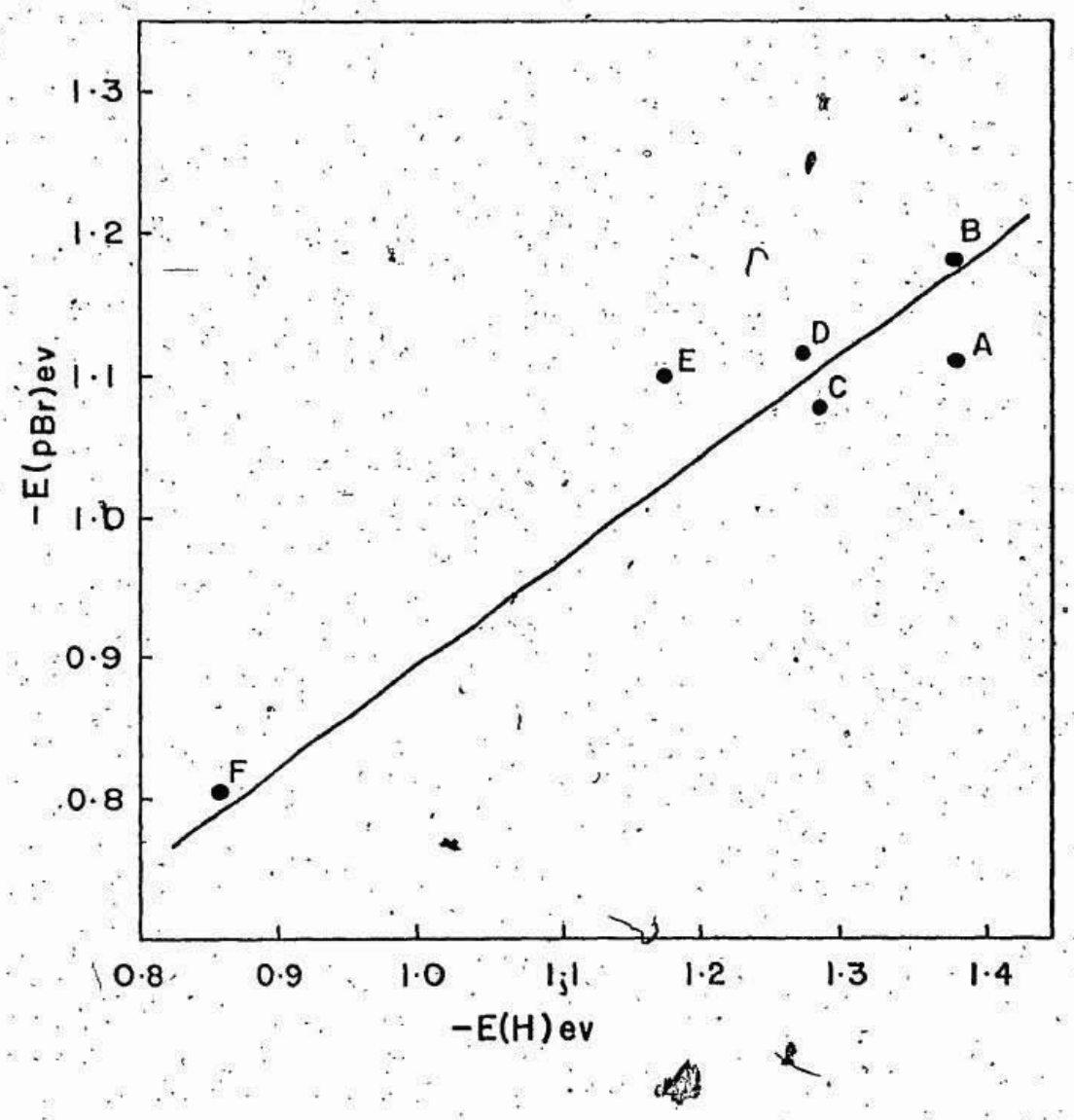


Fig. 5.6 Correlation of half-wave potentials of para-bromo derivatives in Series A to F with those of the corresponding unsubstituted compounds.

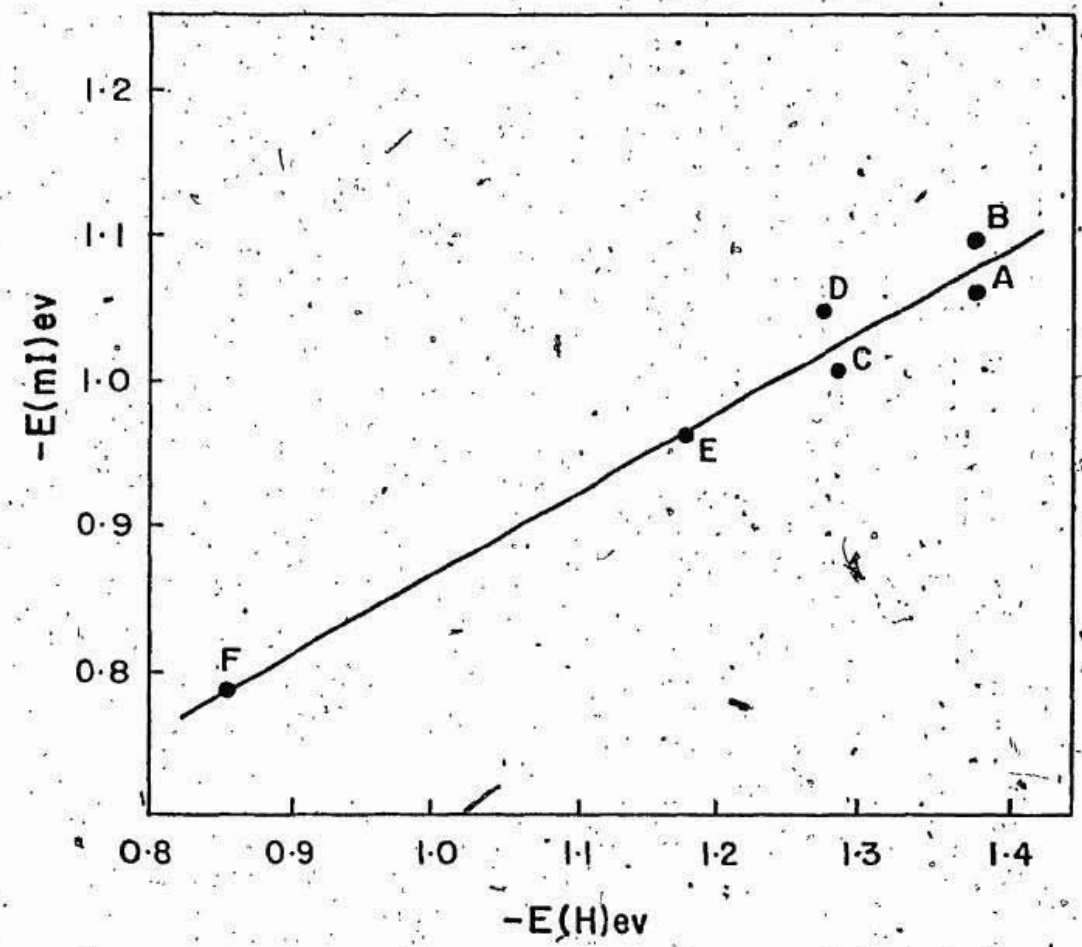


Fig. 5.7 Correlations of half-wave potentials of meta-iodo derivatives in Series A to F with those of the corresponding unsubstituted compounds.

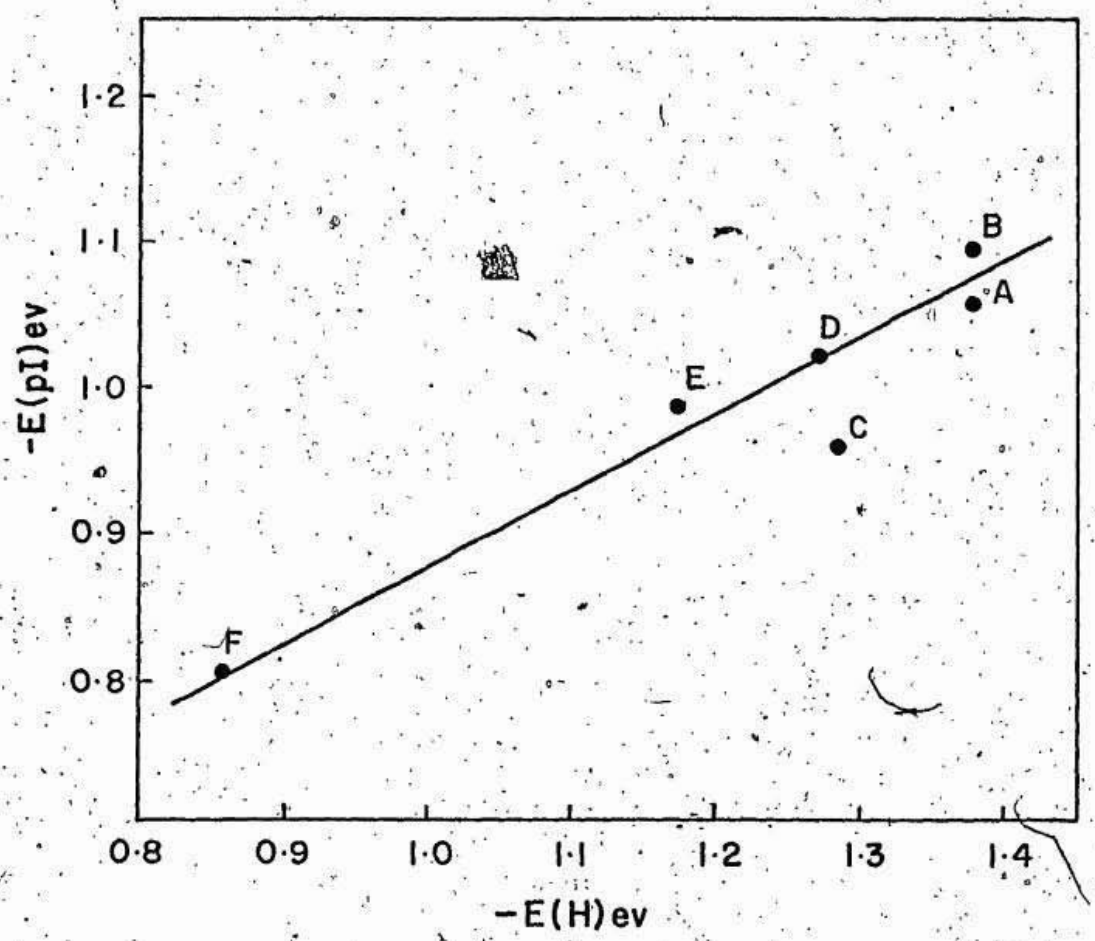


Fig. 5.8 Correlations of half-wave potentials of para-iodo derivatives in Series A to F with those of the corresponding unsubstituted compounds.

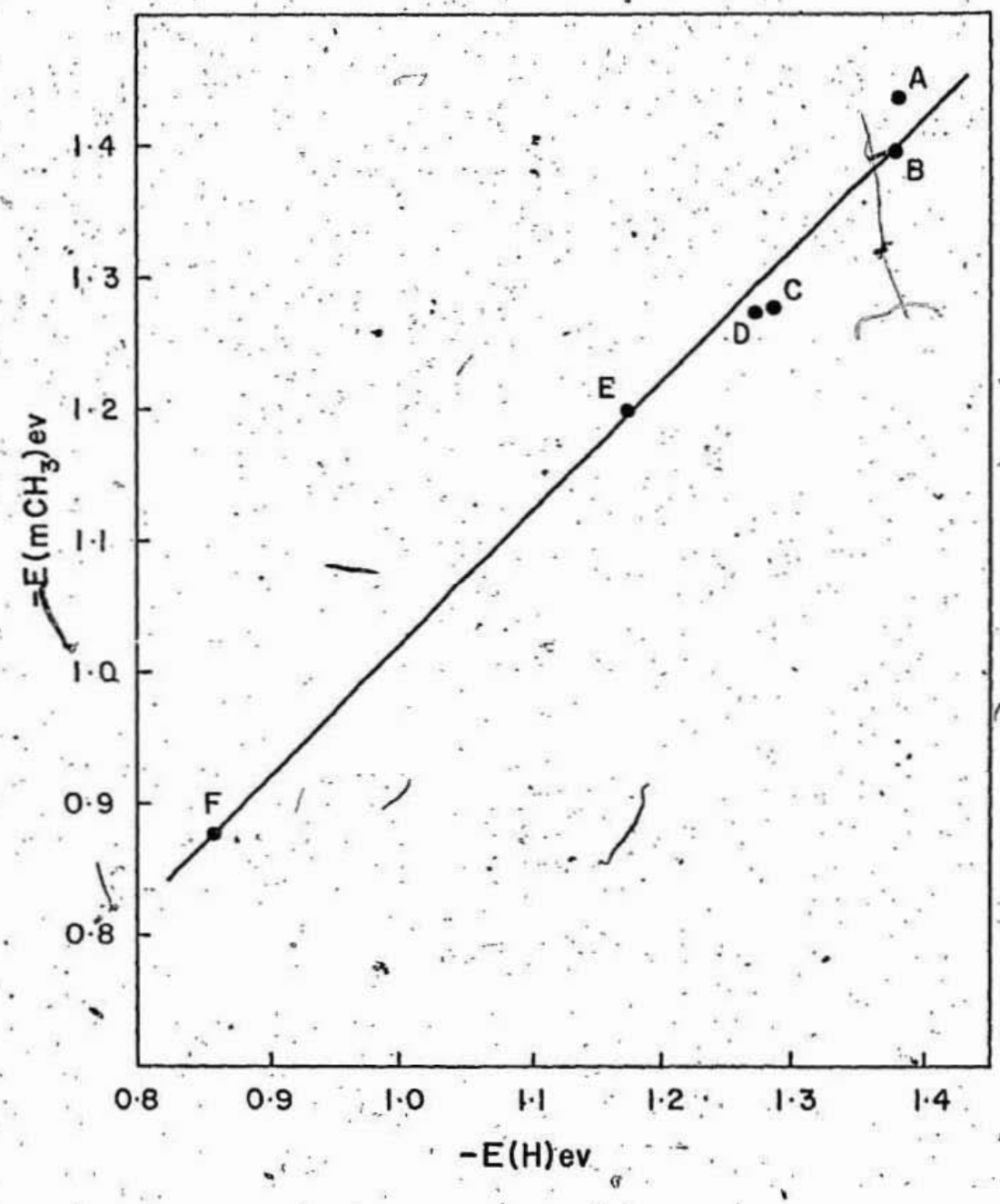


Fig. 5.9 Correlation of half-wave potentials of meta-methyl derivatives in Series A to F with those of the corresponding unsubstituted compounds.

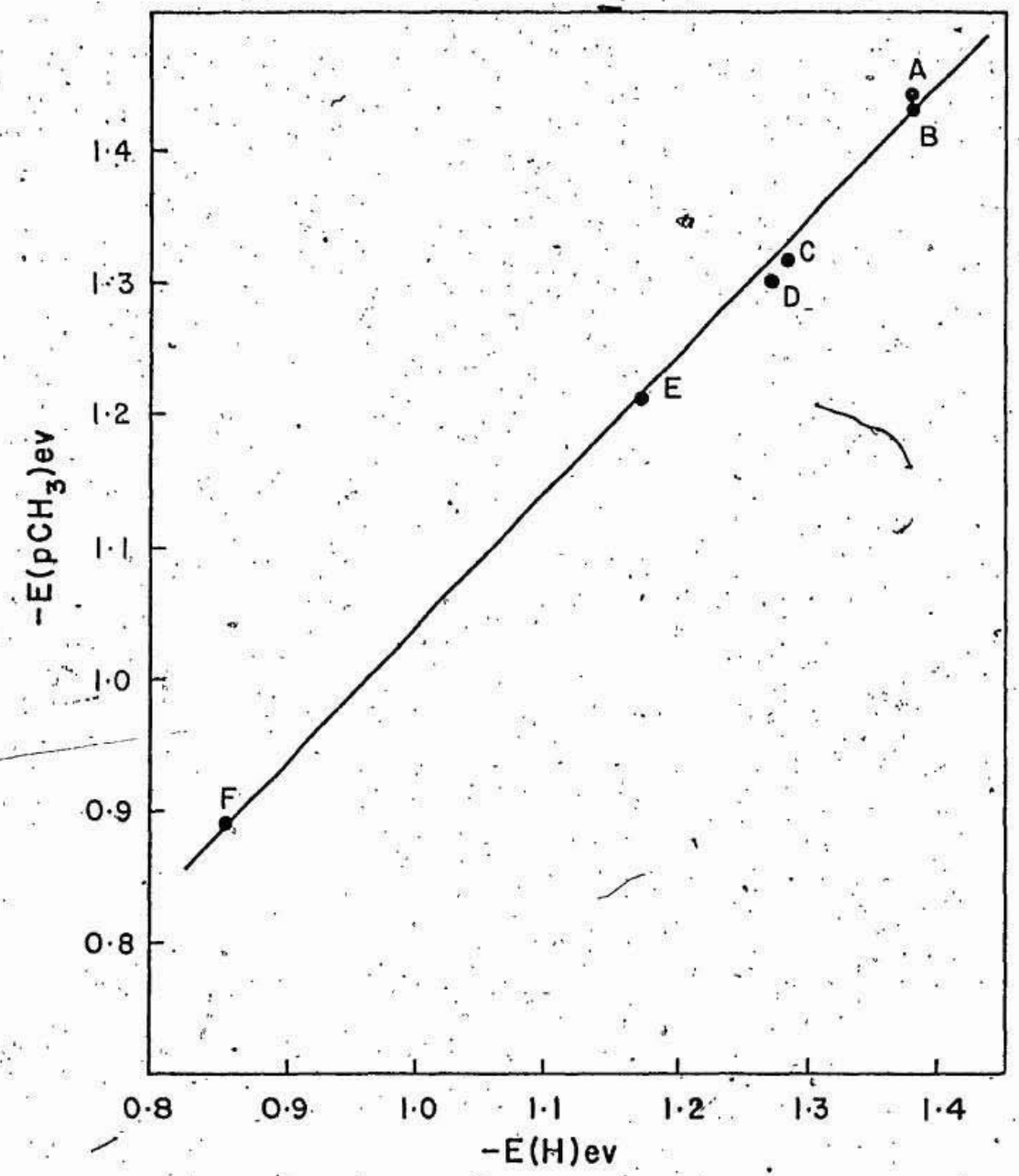


Fig. 5.10 Correlation of half-wave potentials of para-methyl derivatives in Series A to F with those of the corresponding unsubstituted compounds.

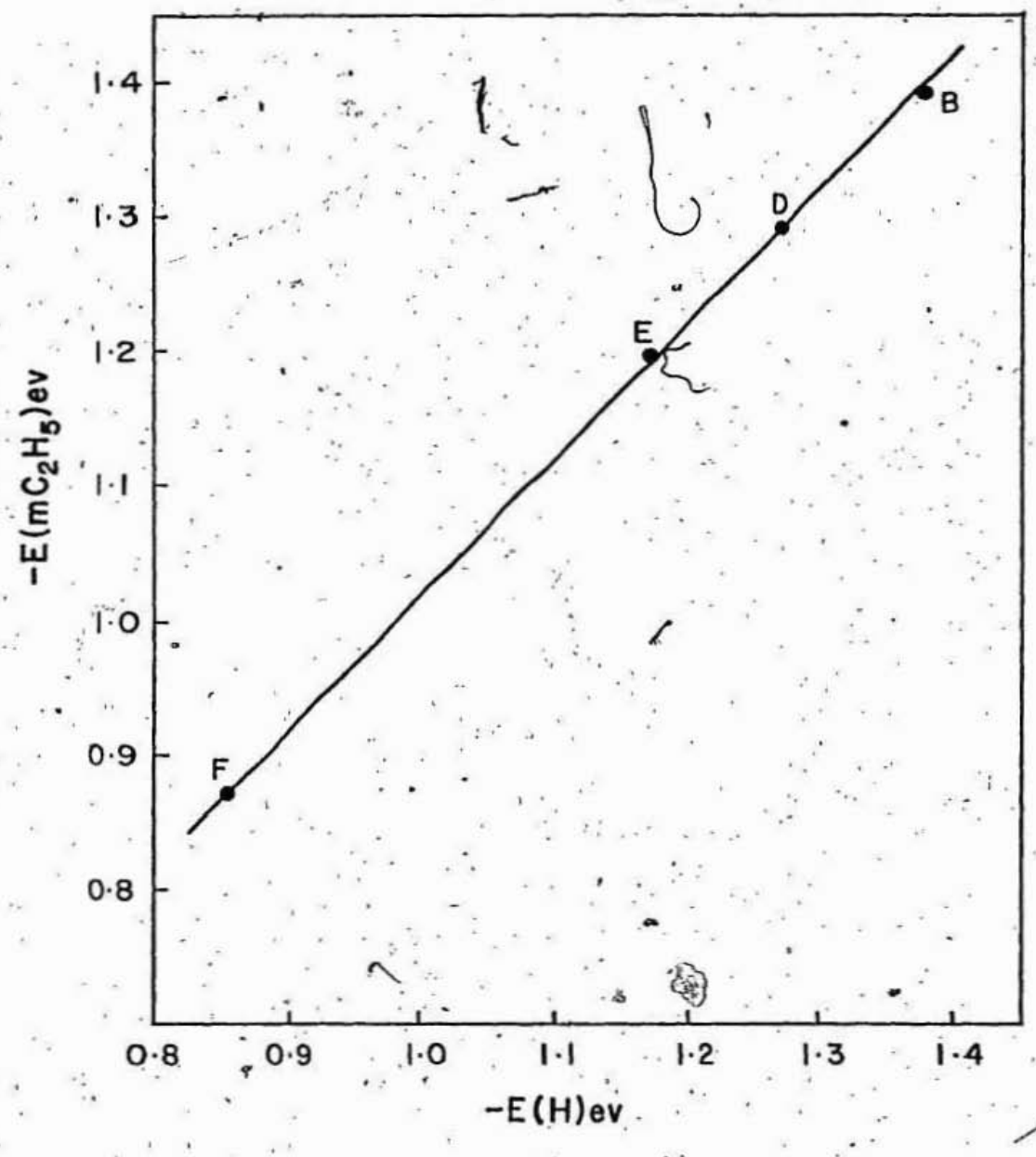


Fig. 5.11 Correlation of half-wave potentials of meta-ethyl derivatives in Series A to F with those of the corresponding unsubstituted compounds.

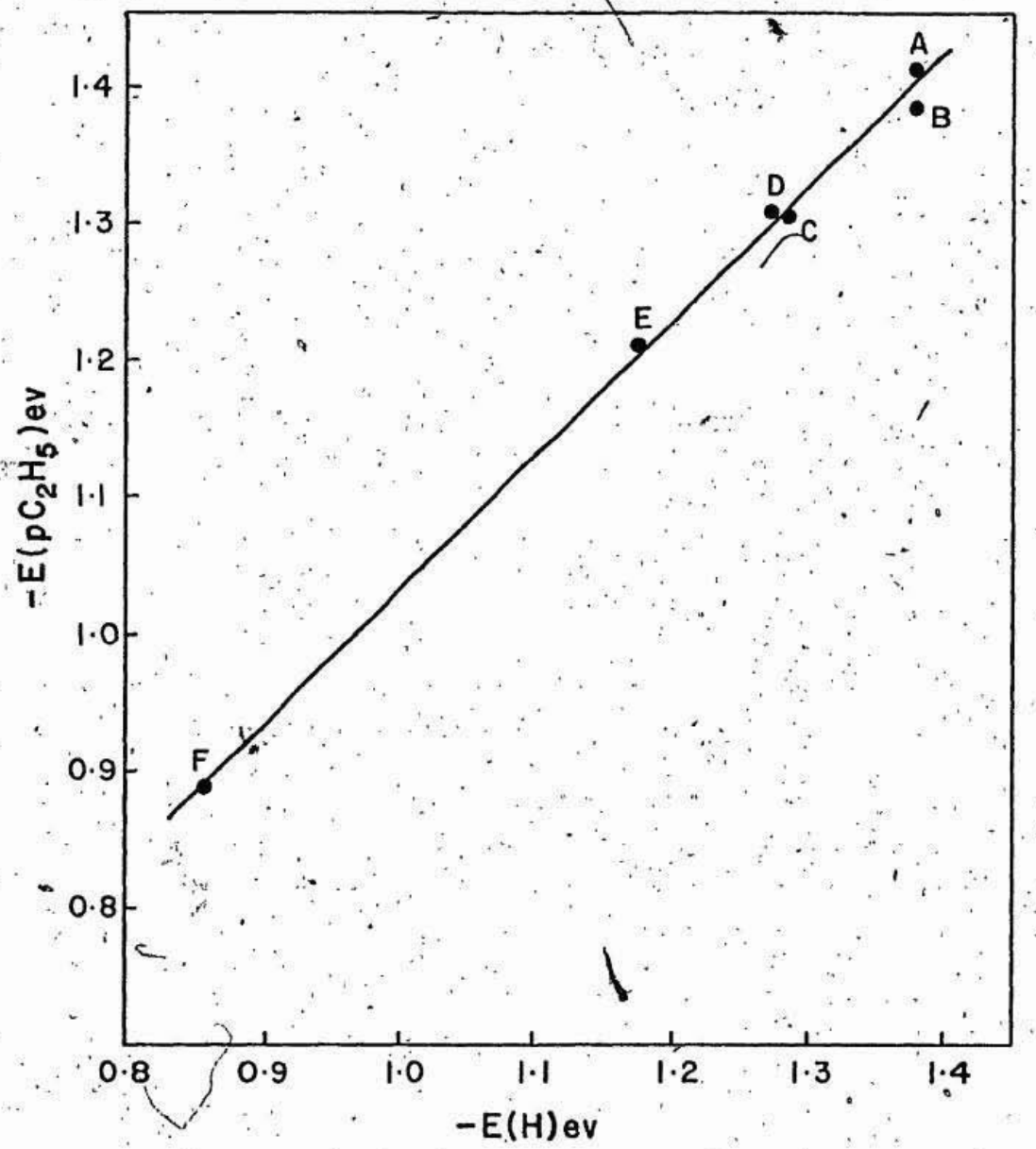


Fig. 5.12 Correlation of half-wave potentials of para-ethyl derivatives in Series A to F with those of the corresponding unsubstituted compounds.

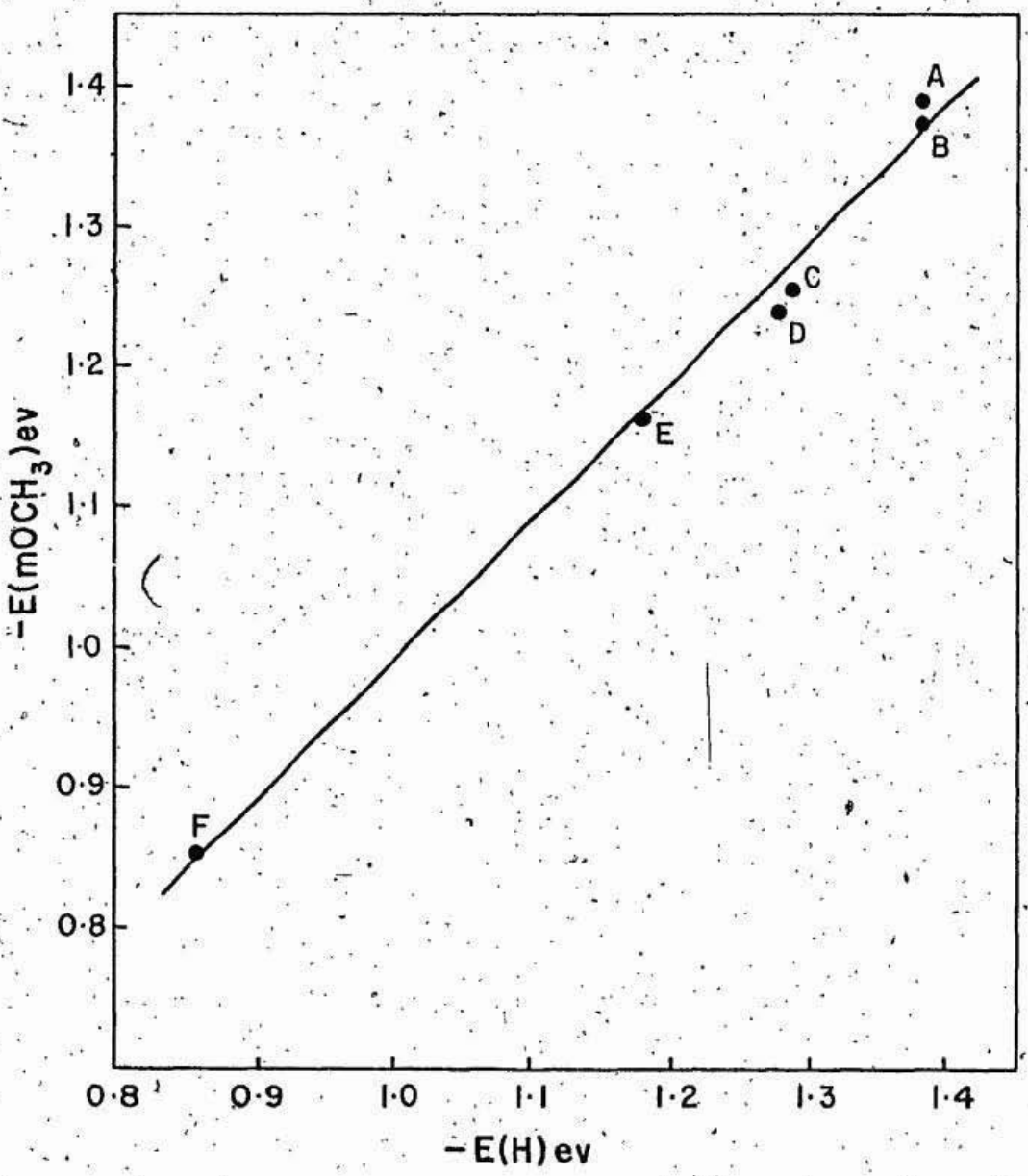


Fig. 5.13 Correlation of half-wave potentials of meta-methoxy derivatives in Series A to F with those of the corresponding unsubstituted compounds.

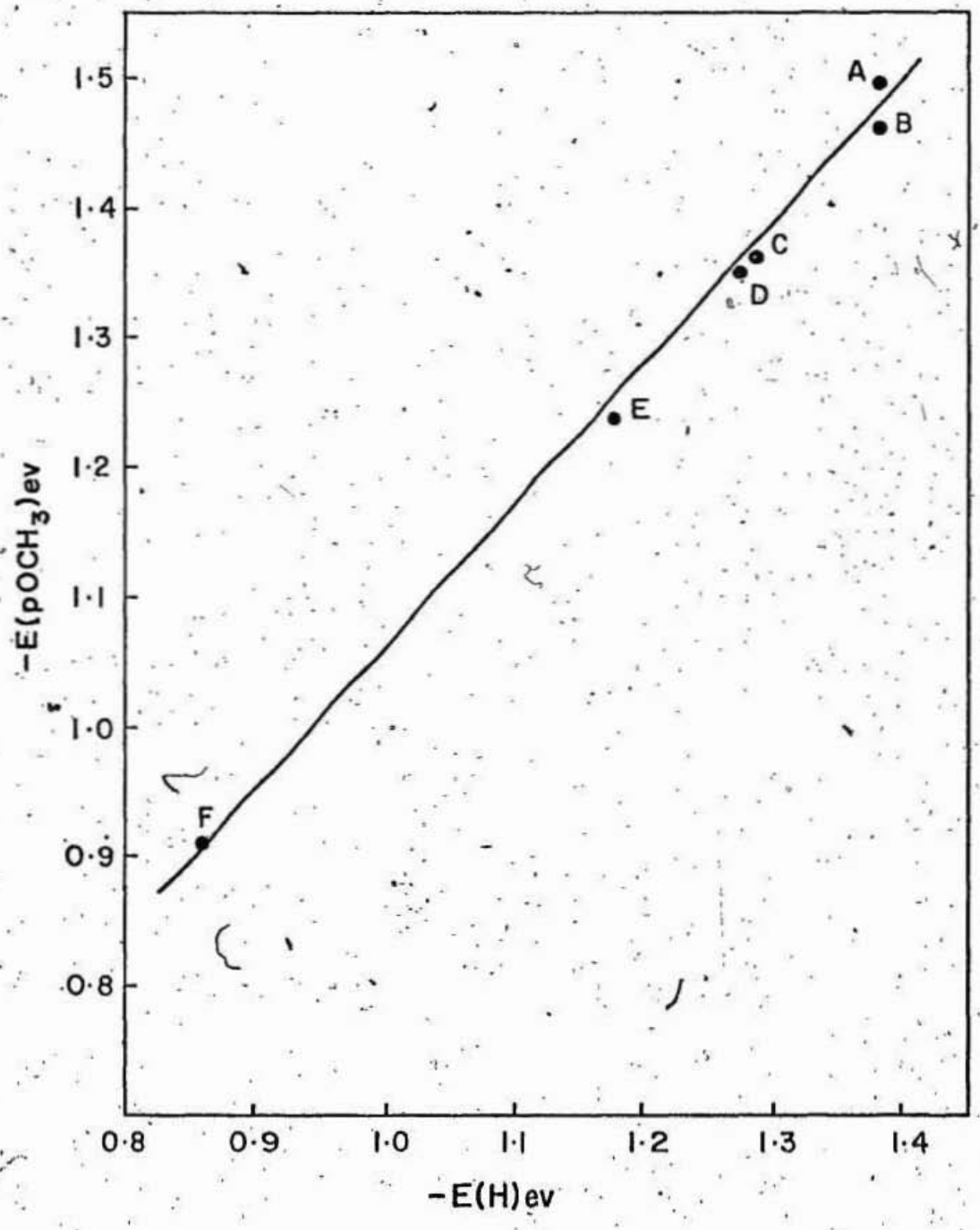


Fig. 5.14 Correlation of half-wave potentials of para-methoxy derivatives in Series A to F with those of the corresponding unsubstituted compounds.

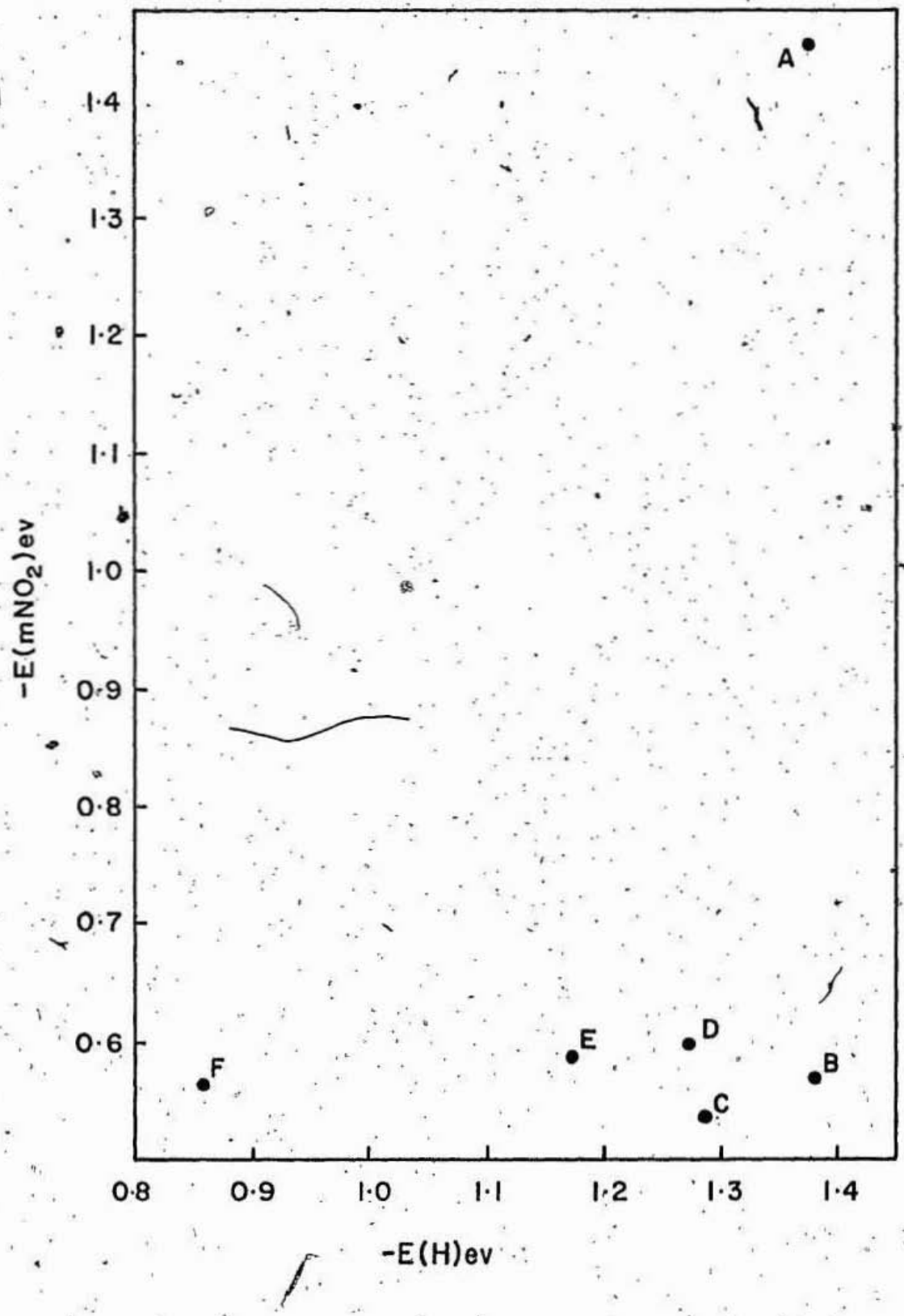


Fig. 5.15 Correlation of half-wave potentials of meta-nitro derivatives in Series A to F with those of the corresponding unsubstituted compounds.

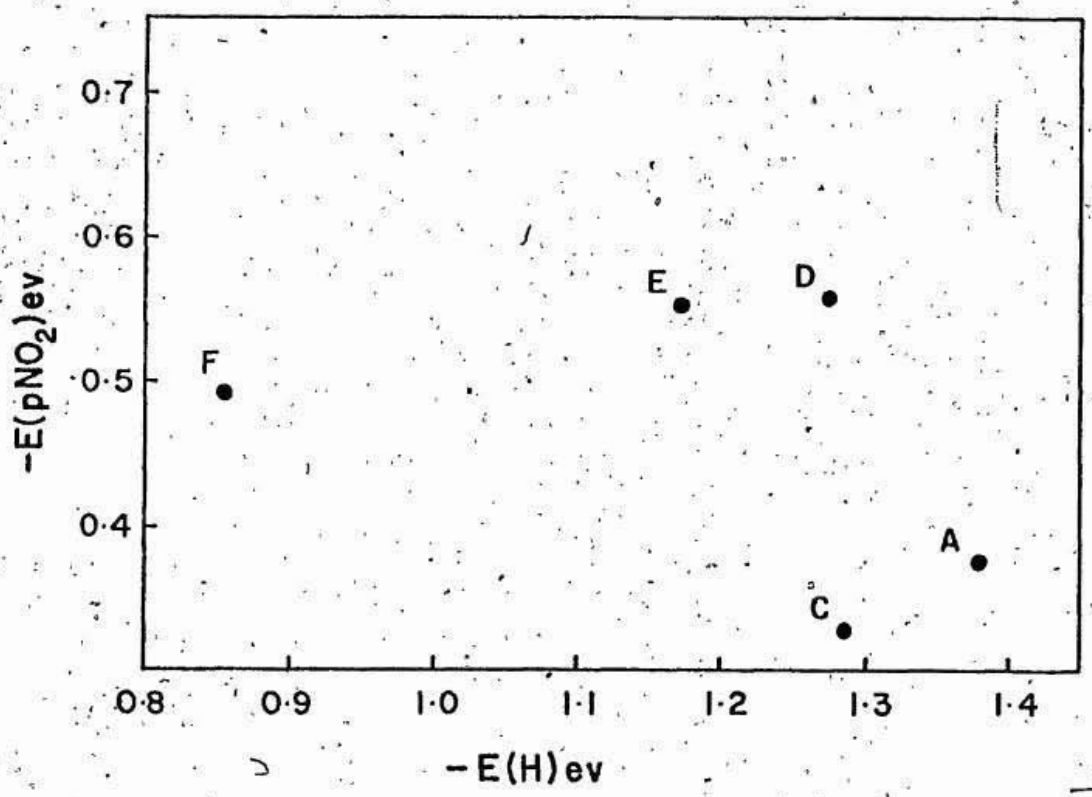


Fig. 5.16 Correlation of half-wave potentials of para-nitro derivatives in Series A to F with those of the corresponding unsubstituted compounds.

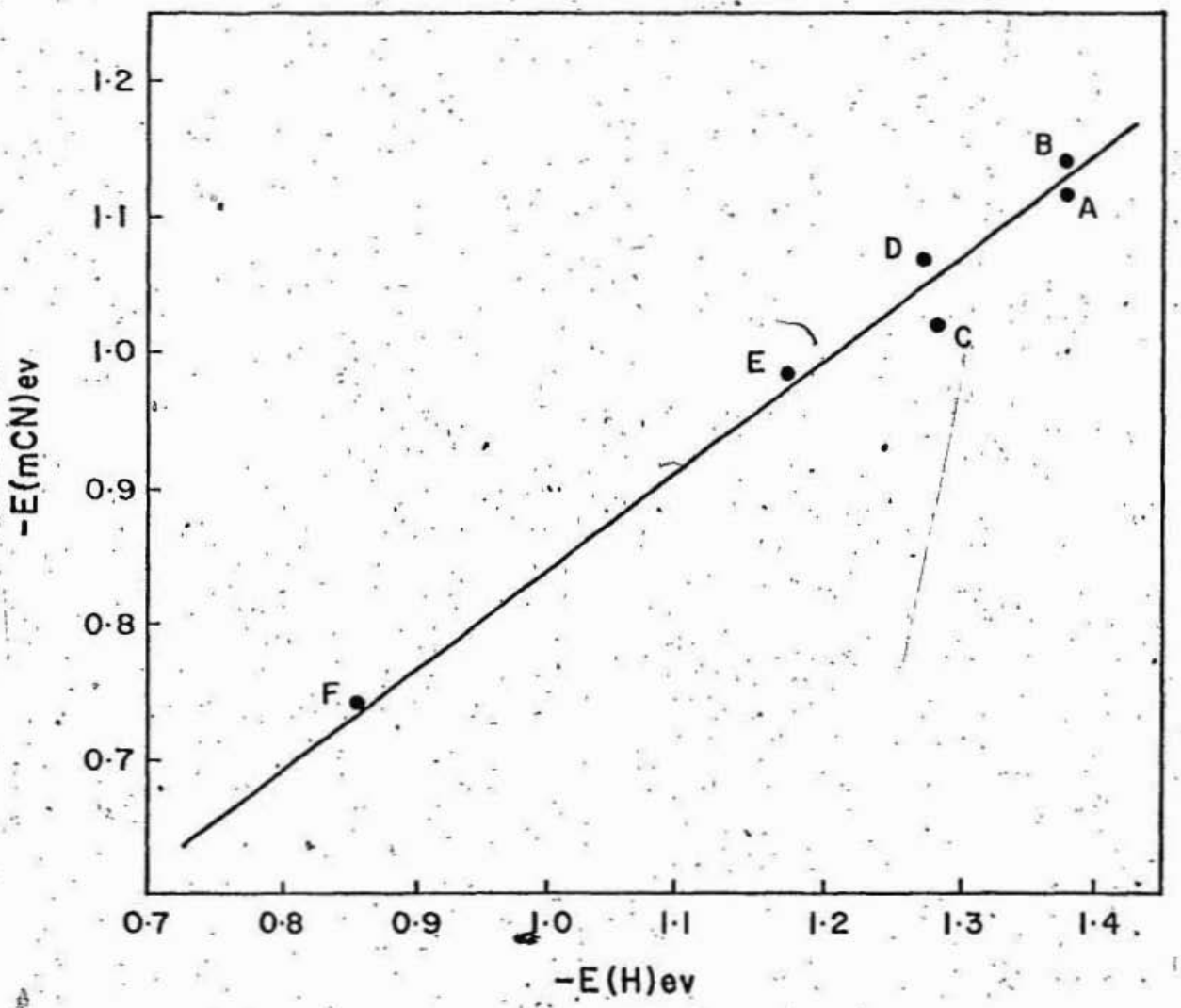


Fig. 5.17 Correlation of half-wave potentials of meta-cyano derivatives in Series A to F with those of the corresponding unsubstituted compounds.

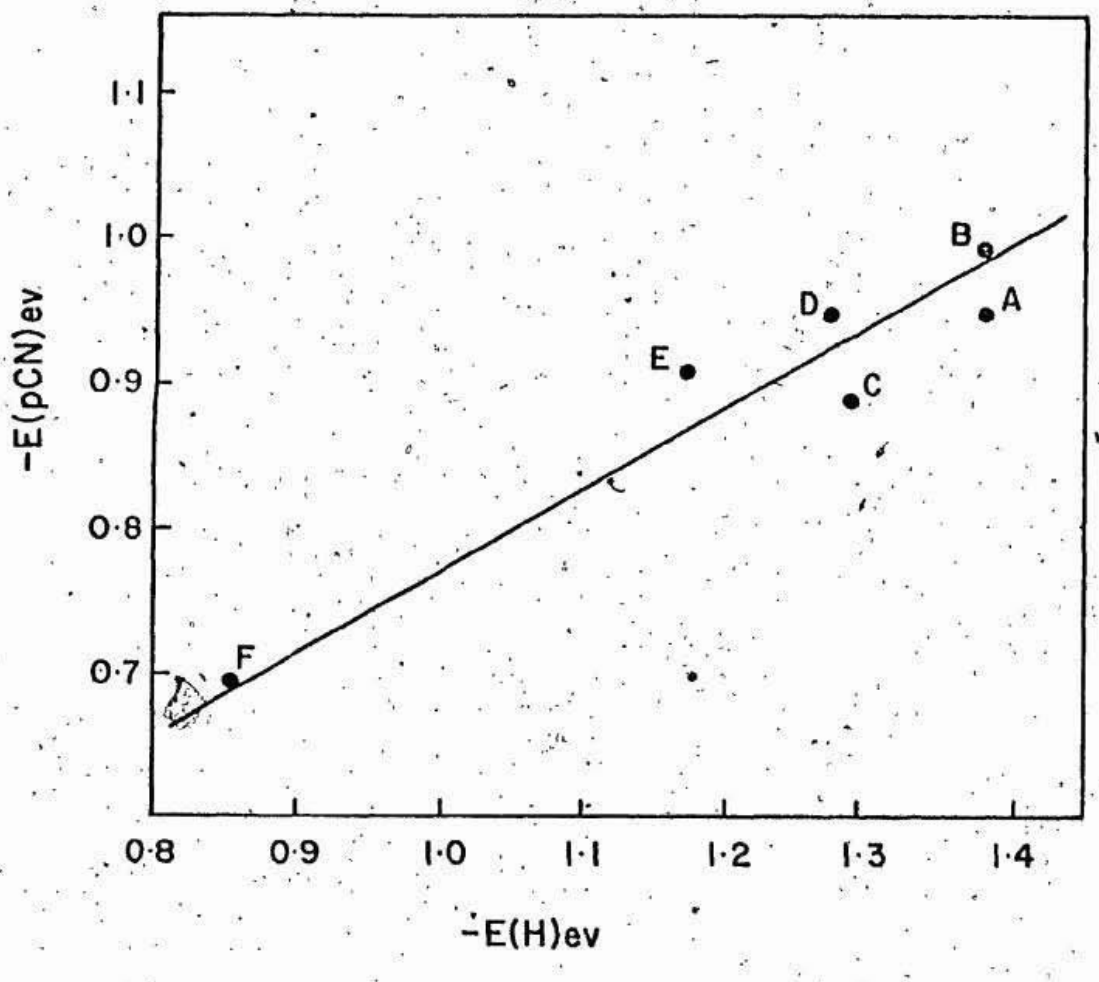


Fig. 5.18 Correlation of half-wave potentials of para-cyano derivatives in Series A to F with those of the corresponding unsubstituted compounds.

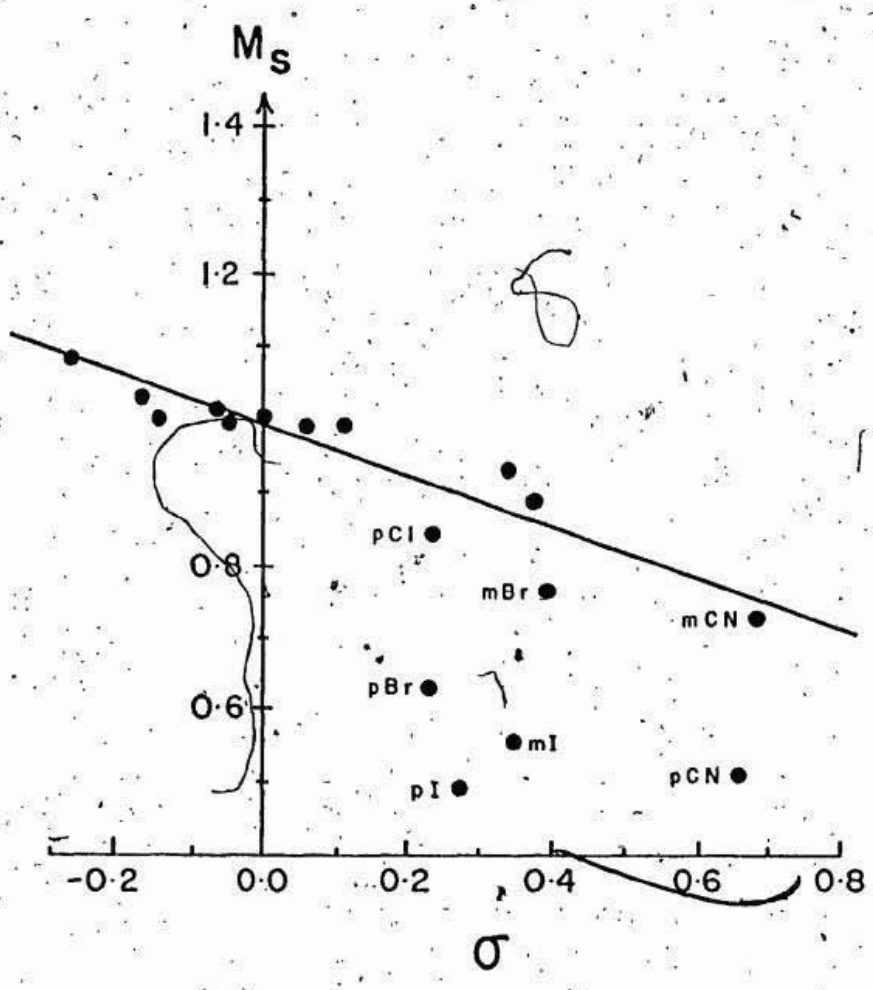


Fig. 5.19 Correlation of the slopes (M_s) of the correlations obtained for substituents in Figs.5.1 to5.18with Hammett's σ values.

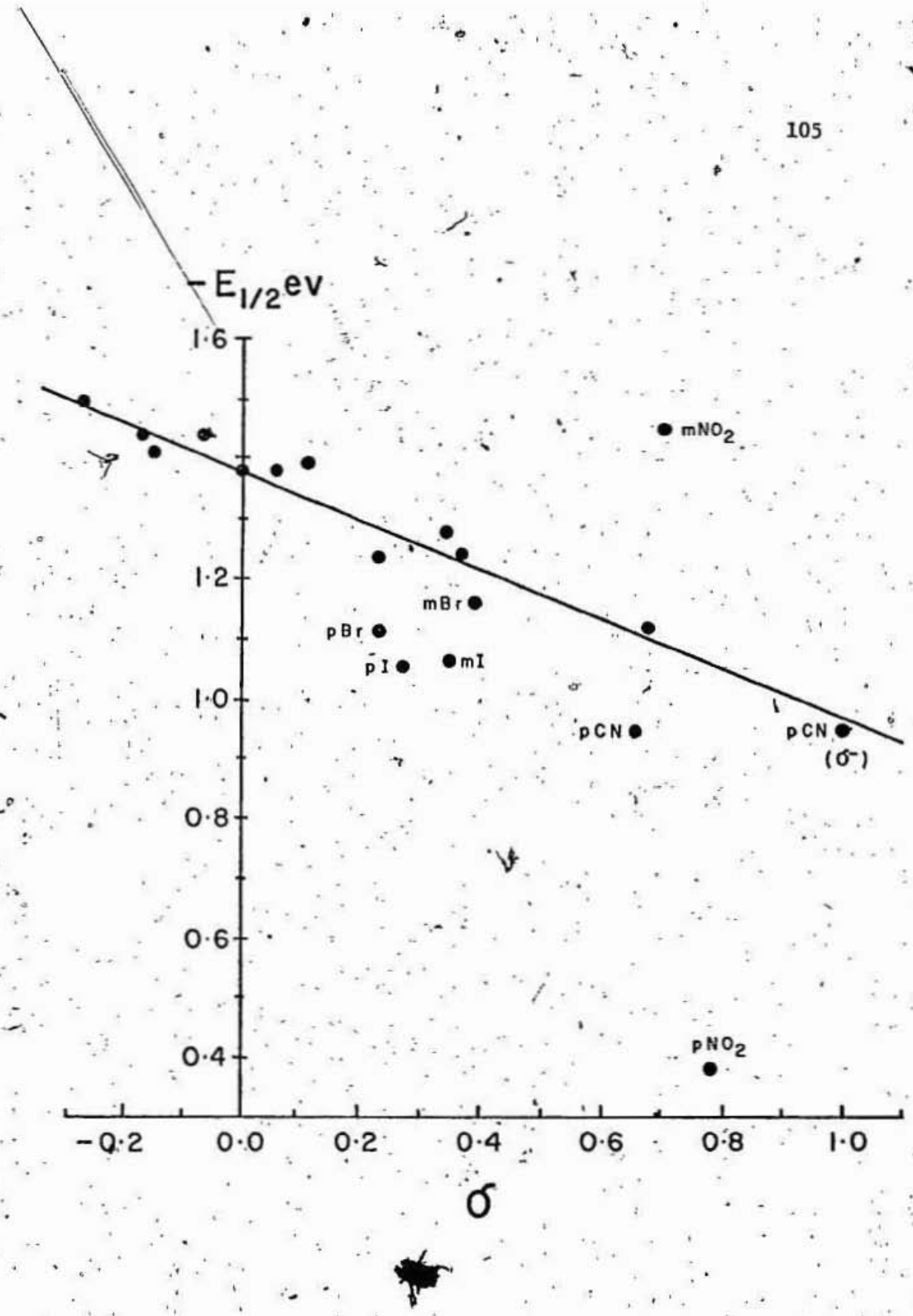


Fig. 5.20 Correlation of half-wave potentials of compounds in Series A with Hammett substituent constants.

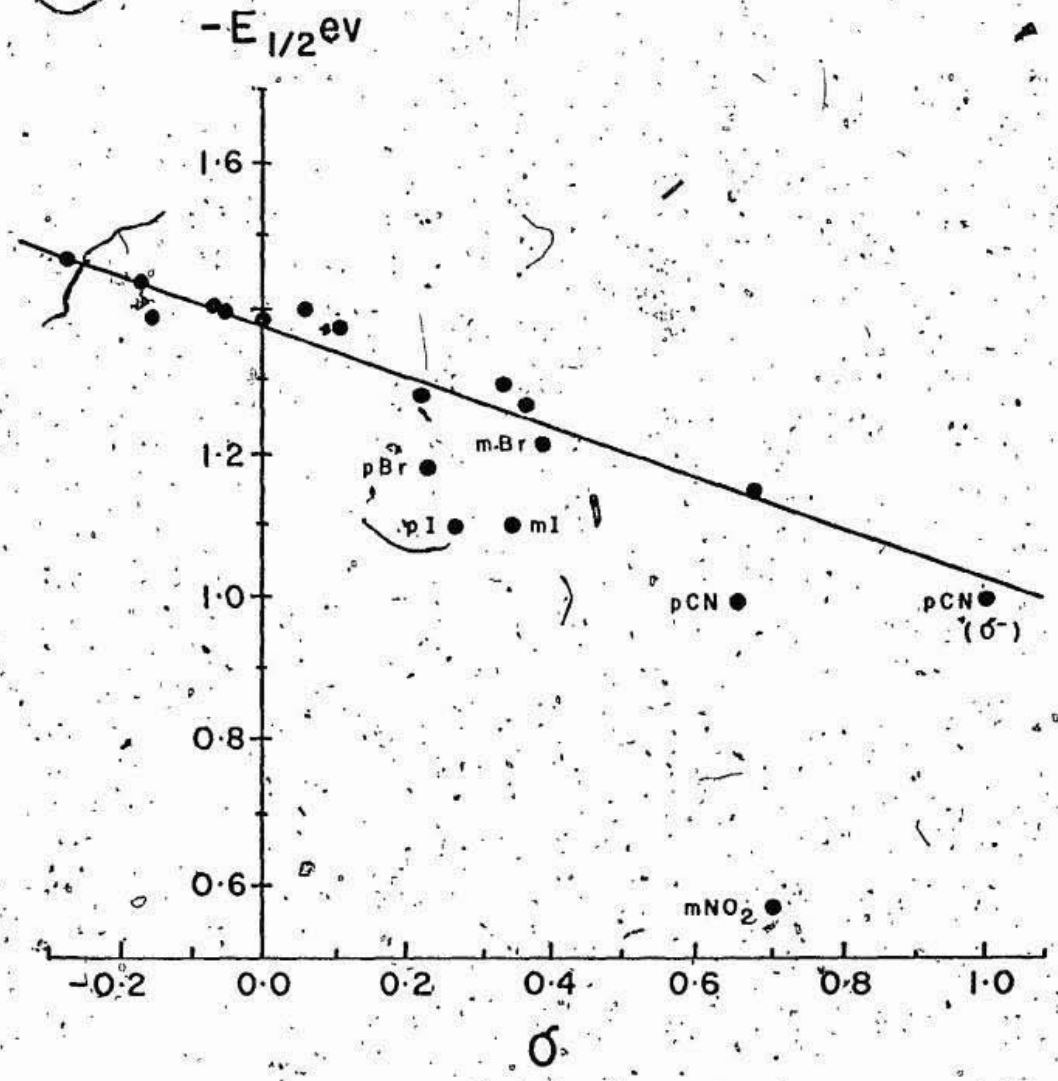


Fig. 5.21 Correlation of half-wave potentials of compounds in Series B with Hammett substituent constants.

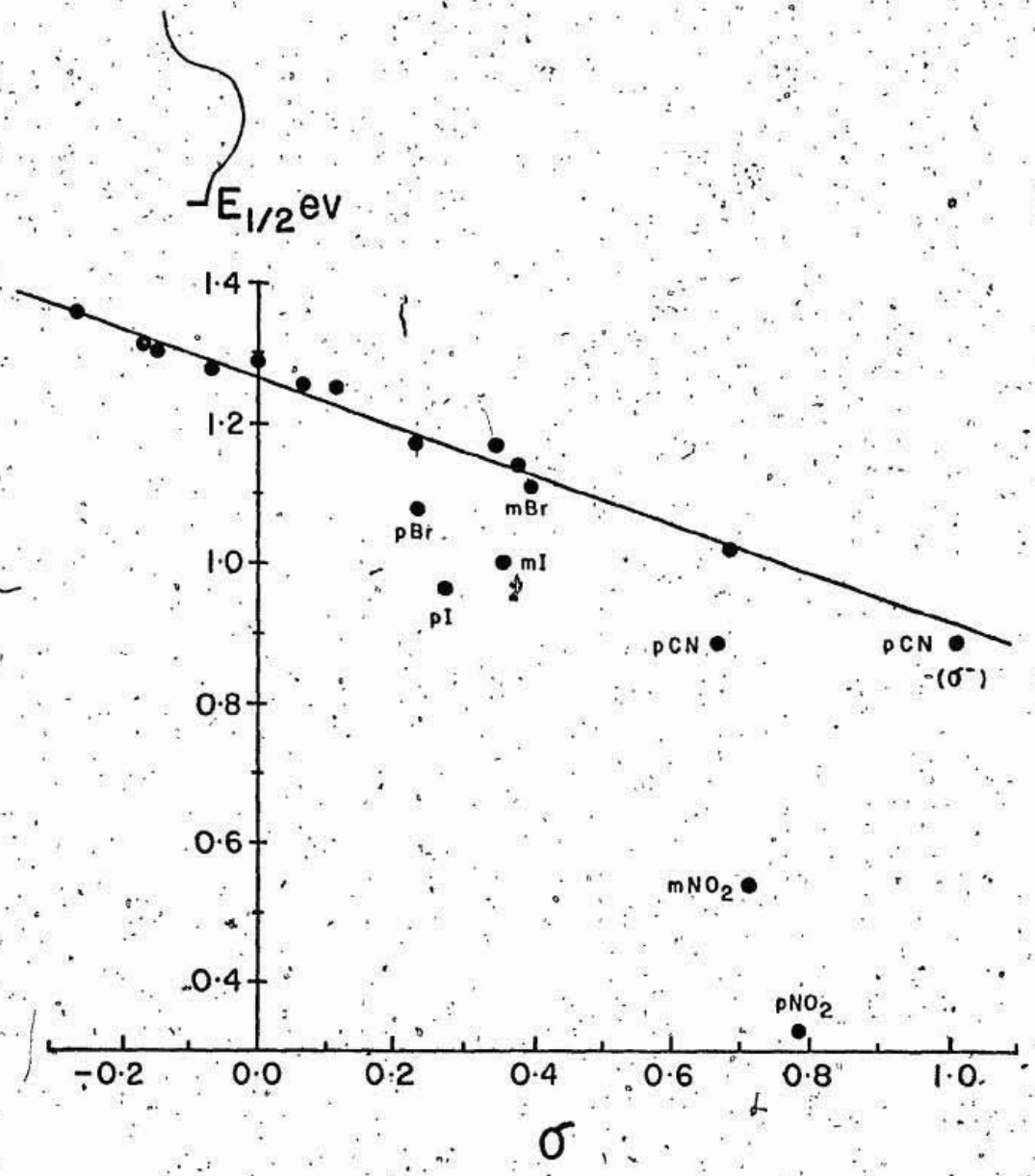


Fig. 5.22 Correlation of half-wave potentials of compounds in Series C with Hammett substituent constants.

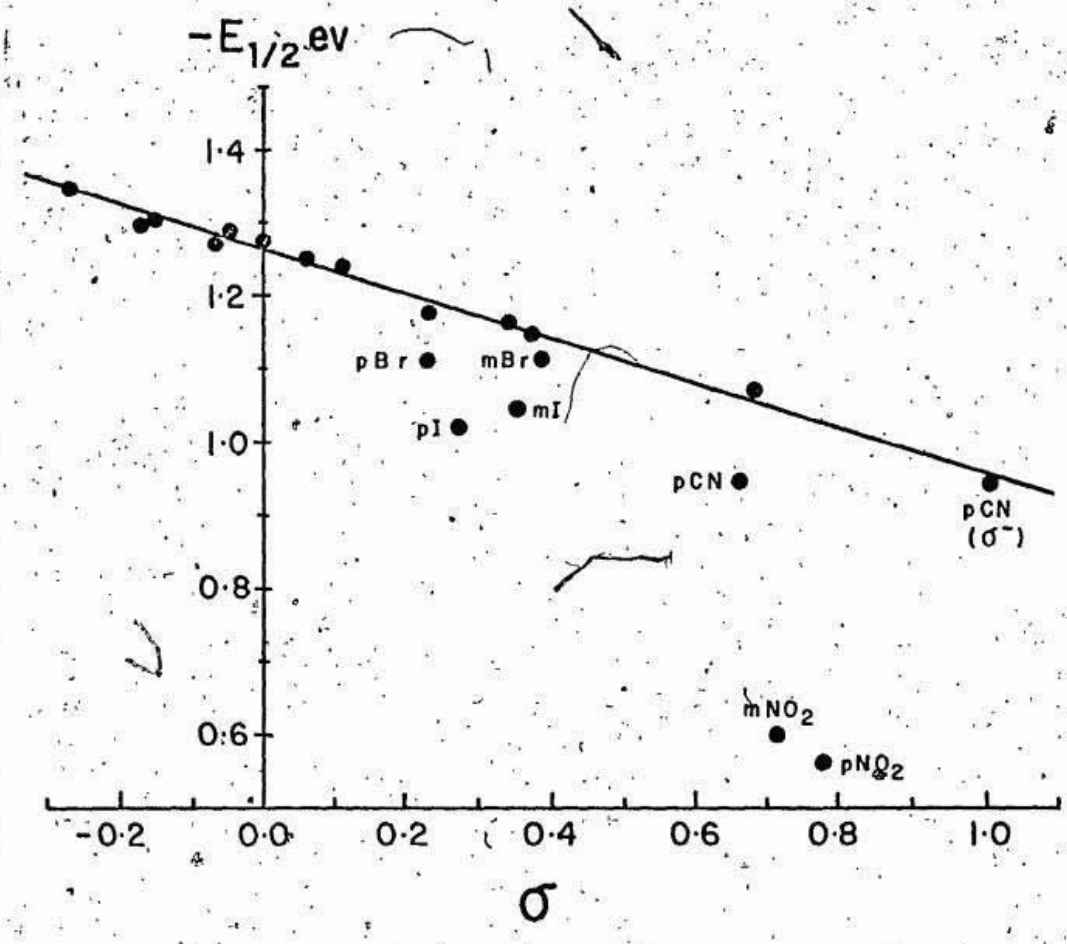


Fig. 5.23 Correlation of half-wave potentials of compounds in Series D with Hammett substituent constants.

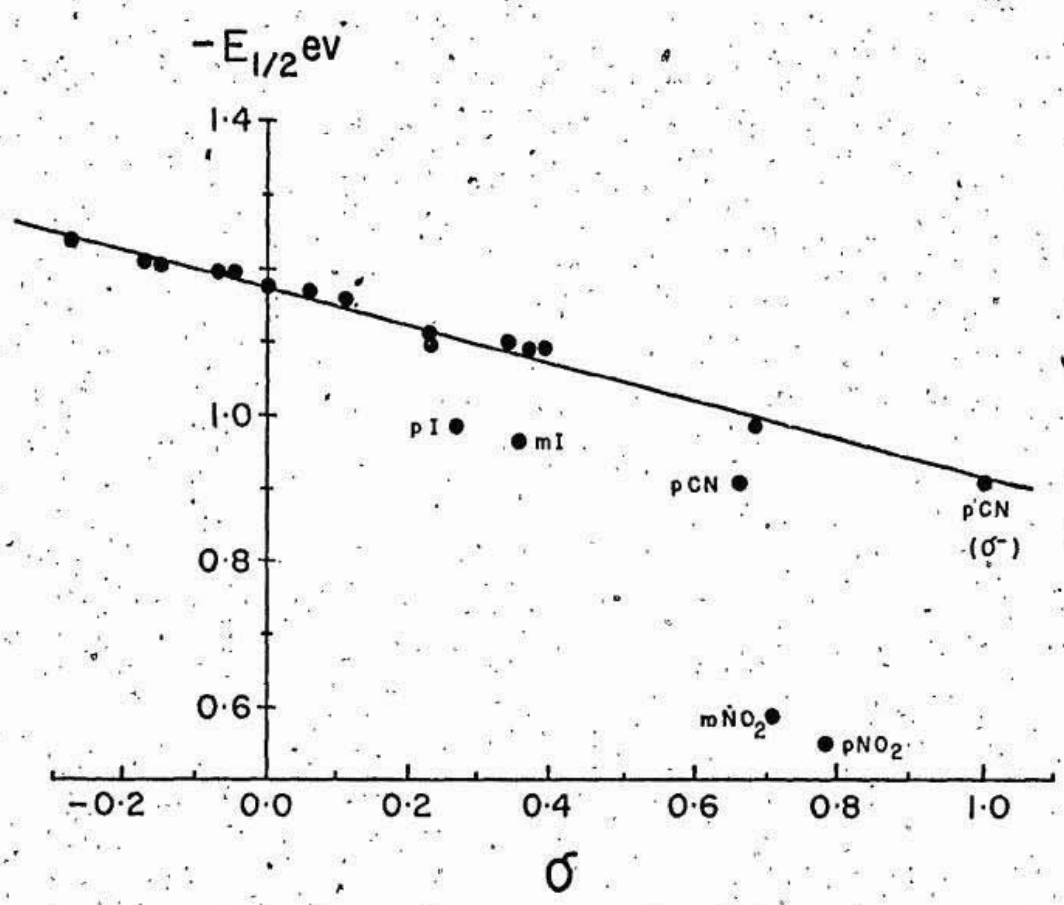


Fig. 5.24 Correlation of half-wave potentials of compounds in Series E with Hammett substituent constants.

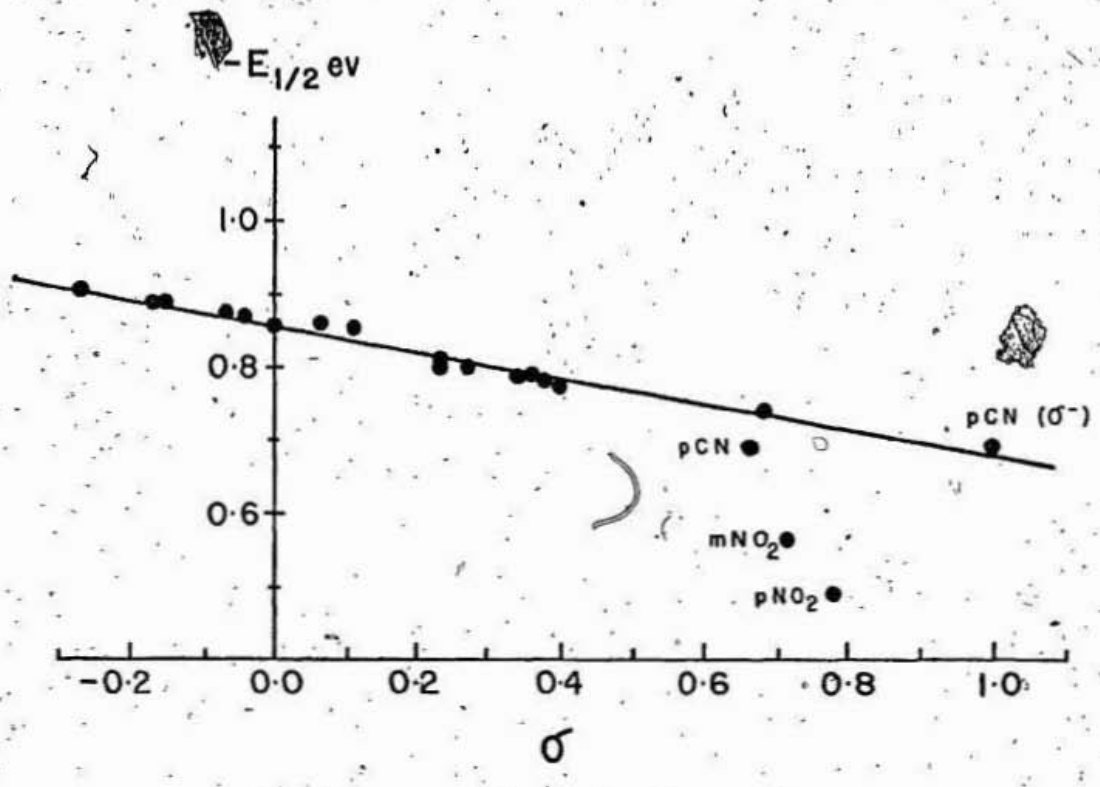


Fig. 5.25 Correlation of half-wave potentials of compounds in Series F with Hammett substituent constants.

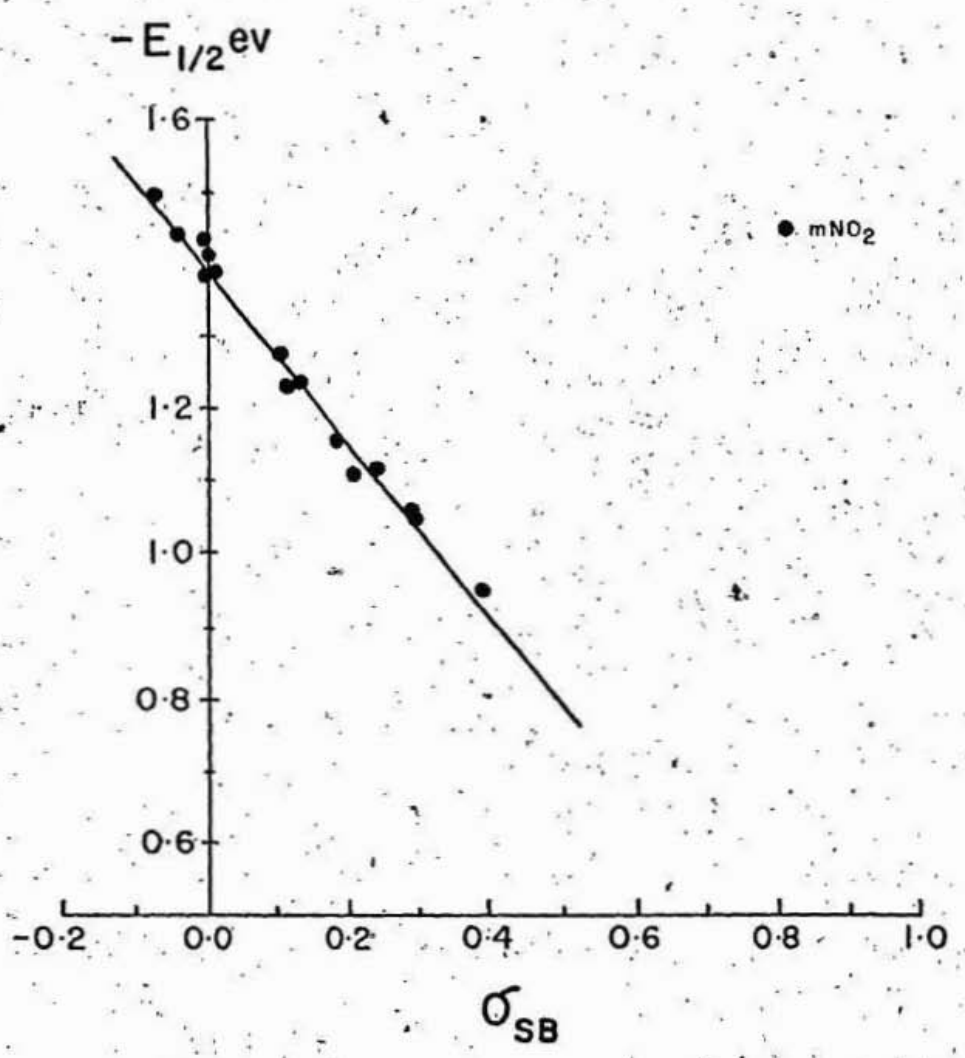


Fig. 5.26 Correlation of half-wave potentials of compounds in Series A with σ_{SB}.

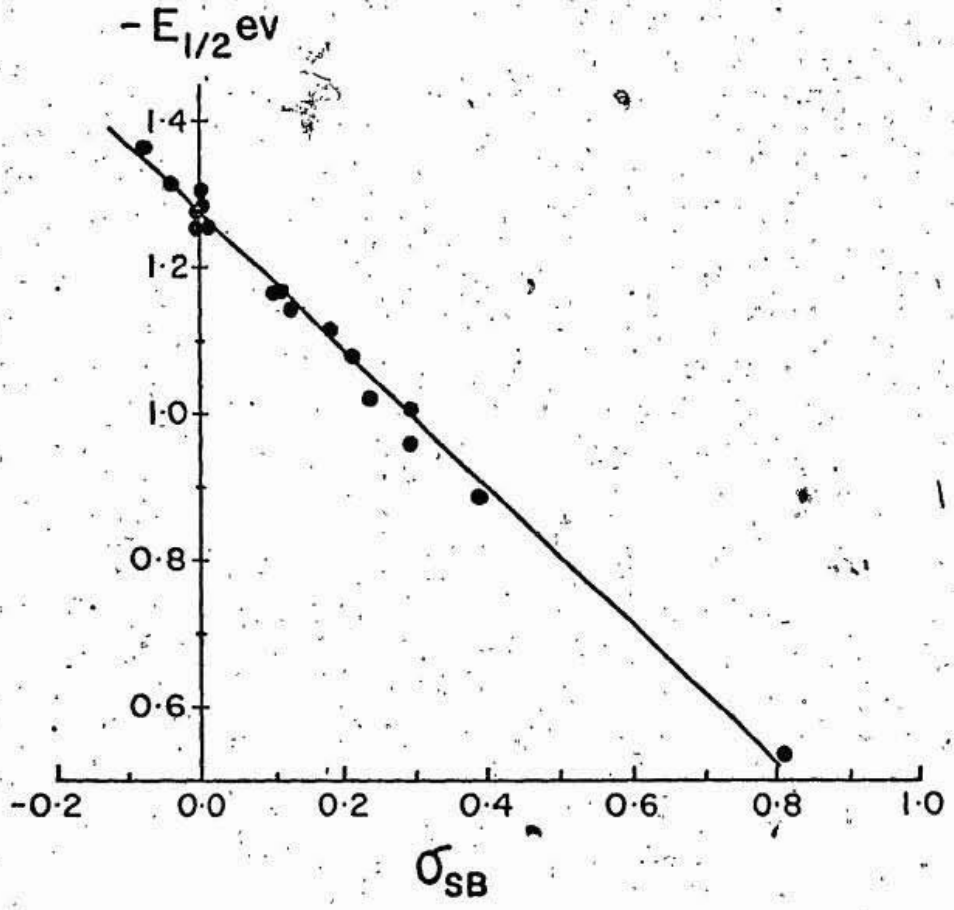


Fig. 5.27 Correlation of half-wave potentials of compounds in Series C with σ_{SB}.

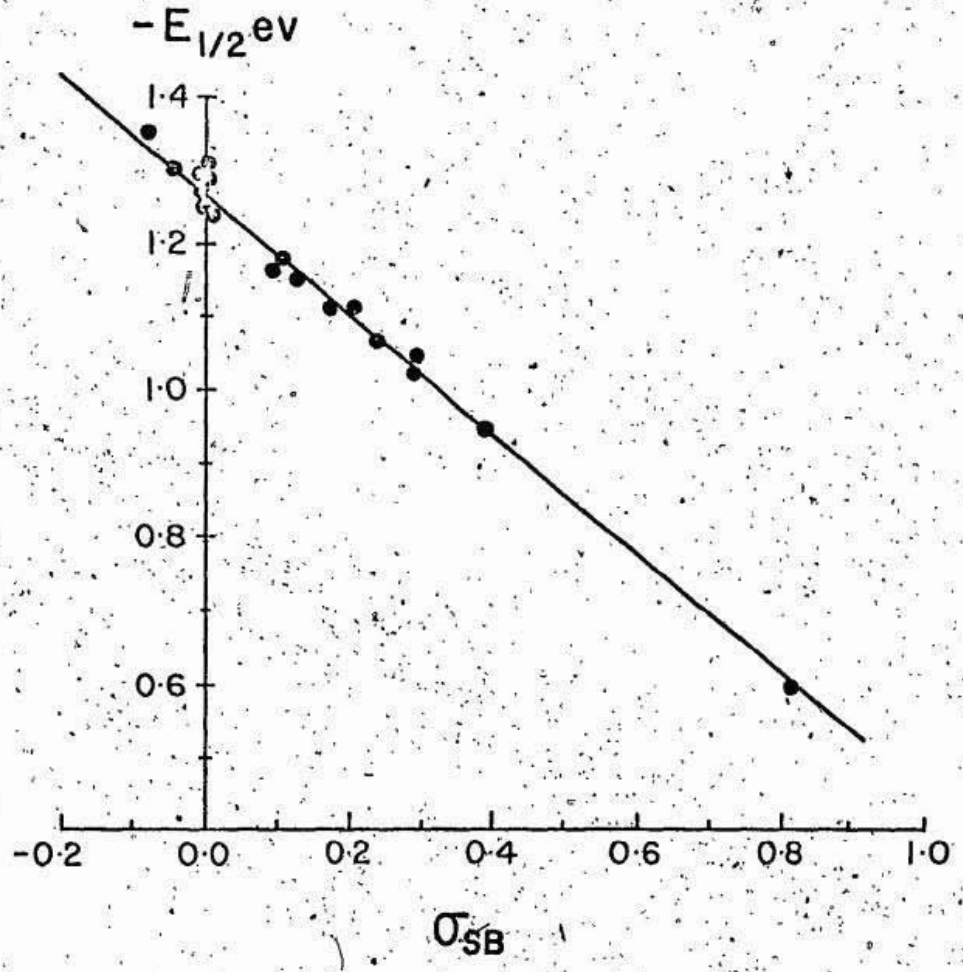


Fig. 5.28 Correlation of half-wave potentials of compounds in Series D with σ_{SB}.

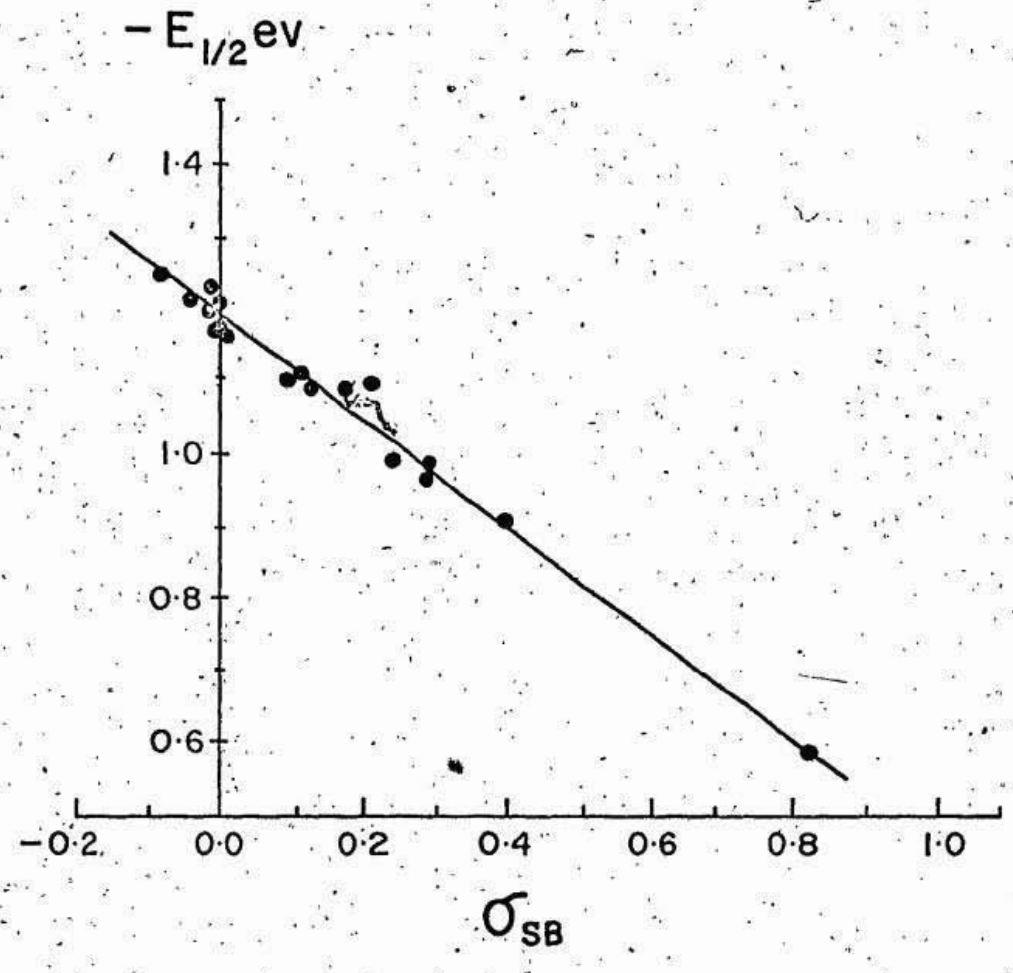


Fig. 5.29 Correlation of half-wave potentials of compounds in Series E with σ_{SB}.

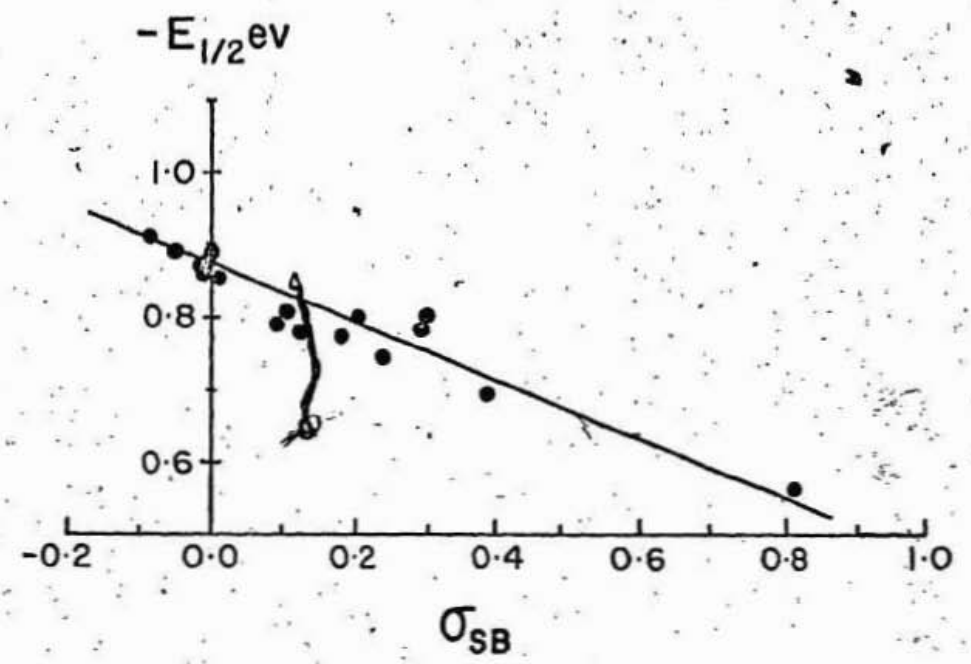


Fig. 5.30 Correlation of half-wave potentials of compounds in Series F with σ_{SB}.

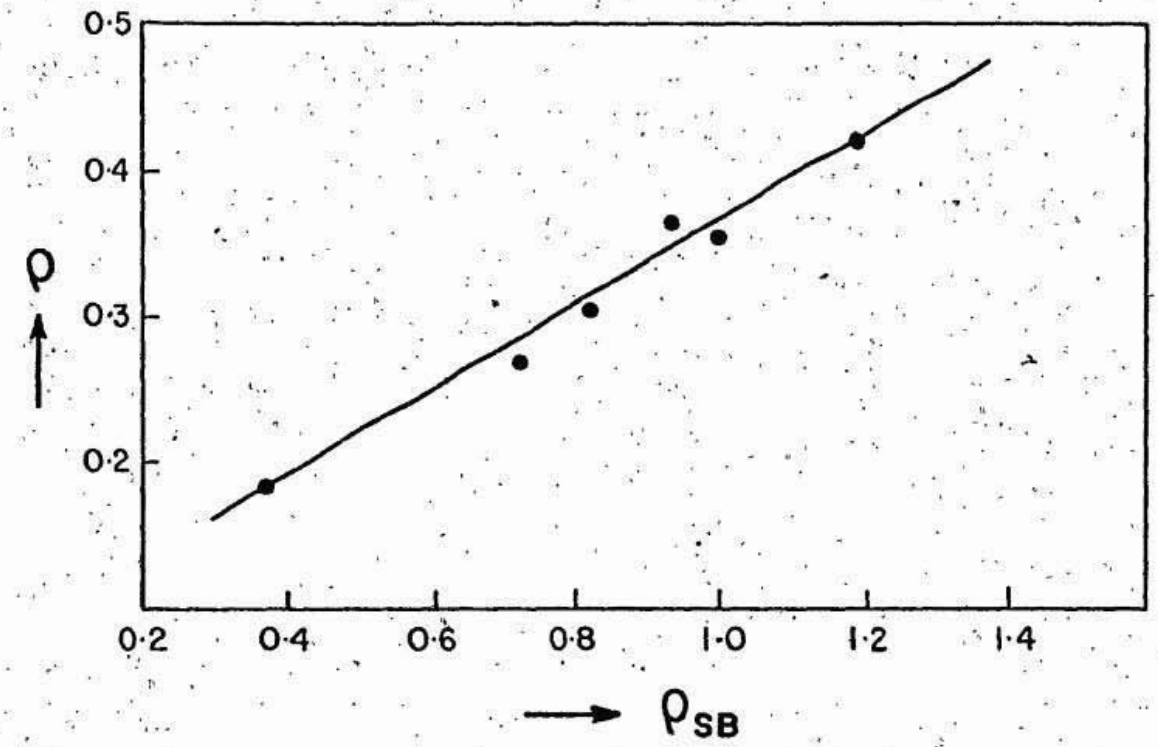


Fig. 5.31 Correlation of the Hammett ρ (Table XXI) with ρ_{SB} (Table XXII).

5.3 Influence of the Aromatic System

Scott and Jura[54] applied the Hückel molecular orbital (H.m.o.) theory to the half-wave potentials of Schiff bases. A number of assumptions were made:

(a) the first step in the reduction process was reversible,

(b) the Schiff bases were in a trans planar configuration, and

(c) the Schiff base structure ArCH = NAr' was equivalent to that of the corresponding hydrocarbon, ArCH = CHAr'. The presence of the nitrogen atom was neglected in the treatment.

The hydrocarbon Ar-CH = CH-Ar', to which the Schiff base, Ar-CH = N-Ar' was considered equivalent, may be considered to be formed from two aryl- methyl radicals, $ArCH_2^{\bullet}$ and $Ar'CH_2^{\bullet}$ respectively. These free radicals combine as follows:

$$ArCH_2^{\bullet} + Ar'CH_2^{\bullet} \longrightarrow ArCH = CHAr' + 2H^{\bullet} . \qquad [36]$$

The non-bonding molecular orbital (n.b.m.o.) coefficients at the extracyclic carbon atoms of the free radicals (a_{or} for $ArCH_2^{\bullet}$ and b_{os} for $Ar'CH_2^{\bullet}$) were used to determine the energies of the highest occupied and lowest unoccupied molecular orbitals of the Schiff bases, which are given by:

$$E \text{ (lowest unoccupied)} = -a_{or}b_{os}\beta \qquad [37]$$

$$E \text{ (highest occupied)} = a_{or}b_{os}\beta \qquad [38]$$

where β is the carbon-carbon resonance integral.

The half-wave potential of a Schiff base corresponds to the energy required to place an electron into the lowest unoccupied molecular

orbital. That is:

$$E_{\frac{1}{2}} = a_{or} b_{os} \beta + C \qquad [39]$$

where C' is a constant. In spite of the assumptions made above, particularly the assumed equivalence of the carbon and nitrogen atoms, Equation [39] accommodated Scott's and Jura's experimental data satisfactorily.

Considering the data presented in this thesis, two kinds of correlation are possible between the standard series (Series B) and the other series of Schiff bases.

(a) Series B can be correlated with Series A and C, in which the substituents are on the aldehyde portion of the molecule.

(b) Series B can be correlated with Series D, E and F, in which the substituents are on the amine portion of the molecule.

The correlations of Series B with Series A and C, are not amenable to any simple theoretical interpretation. However, correlations of Series B with Series D, E and F can be treated further in terms of Equation [39], as follows. Combining Equation [34] with Equation [39], we have:

$$\sigma_{SB} = a_{or}(B) b_{os}(X) \beta - a_{or}(B)\, b_{os}(H) \beta \,. \qquad [40]$$

$$= a_{or}(B) \beta \{ b_{os}(X) - b_{os}(H) \} \qquad [41]$$

where $a_{or}(B)$ is the n.b.m.o. coefficient for the extracyclic carbon atom in a benzyl radical and where $b_{os}(X)$ values are the "effective" n.b.m.o. coefficients for the amine fragments of the Schiff bases. Since $b_{os}(H)$ and β are constants, Equation [40] can be written in

the form:

$$\sigma_{SB} = a_{or}(B)\, b_{os}(X)\, \beta + C' \qquad [42]$$

Applying Equation [39] to the correlation between Series D and σ_{SB}, we have:

$$E_{\frac{1}{2}}(D) = a_{or}(D)\, b_{os}(X)\, \beta + C'' \qquad [43]$$

where $a_{or}(D)$ is the n.b.m.o. coefficient for the extracyclic carbon of the 2-naphthyl radical. Combining Equations [42] and [43], with the elimination of term $b_{os}(X)\beta$ gives:

$$E_{\frac{1}{2}}(D) = a_{or}(D)/a_{or}(B)\, \sigma_{SB} + C''' \qquad [44]$$

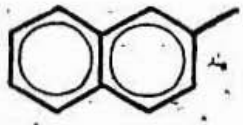
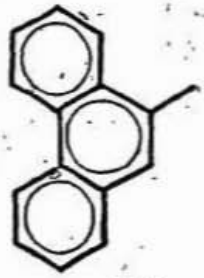
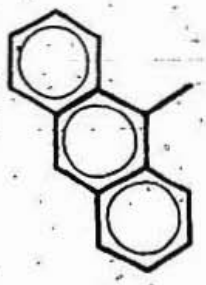
which may be written:

$$E_{\frac{1}{2}}(D) = \rho(D)\, \sigma_{SB} + C''' \qquad [45]$$

where $\rho(D) = a_{or}(D)/a_{or}(B)$.

The values of the a_{or} terms, calculated for the extracyclic carbon atoms of the aldehyde fragments of the Schiff bases in Series B, D, E and F are recorded in Table XXIII. These theoretical ρ values should correlate with the experimentally determined ρ_{SB} values recorded in Table XXII. Since $a_{or}(B)$ is a constant factor in all the theoretical ρ values, a plot of the experimental ρ_{SB} values against the values of a_{or} for the corresponding aldehyde fragments of the Schiff bases should give a straight line. This correlation is illustrated in Fig. 5.32. A least squares analysis of the data gives the equation:

Table XXIII Approximate Values of a_{or} for the Aldehyde Fragments of the Schiff bases in Series B, D, E and F

Series	Aldehyde fragment	a_{or}
B		.7558
D		.7275
E		.6680
F		.5346

$$a_{or} = (0.368 \pm 0.044)\rho_{SB} + (0.404 \pm .034) \quad [46]$$

In the Scott and Jura[54] treatment, no specific consideration of the nitrogen atom was made and, on this basis, the following relationship between Schiff bases prepared from the same parent aldehyde and different amines was established:

$$E_{\frac{1}{2}}(a) = AE_{\frac{1}{2}}(b) + B \quad [47]$$

where A and B are constants and $E_{\frac{1}{2}}(a)$ and $E_{\frac{1}{2}}(b)$ are the half-wave potentials of the corresponding Schiff bases derived from two different amines.

A further development by Benson and Scott[87] considered the presence of the nitrogen atom. With R and S being odd alternant hydrocarbon radicals, the changes R + S → RS → SB were treated by first order perturbation theory to give the following equation for the energy of the lowest unoccupied orbital of the Schiff base:

$$E_{SB}^{+} = - a_{or} b_{os} k_{CN} \beta + \tfrac{1}{2}(b_{os})^2 h_N \beta \quad [48]$$

where a_{or}, b_{os} are the n.b.m.o. coefficients of atom r at R and atom s of S, and where k_{CN} and h_N are parameters which refer to the alterations which occur in the resonance and coulombic integrals when carbon is replaced by nitrogen.

Two kinds of correlations appear possible on the basis of Equation [47], depending on whether the amine fragment or the aldehyde fragment is constant. The treatment of Benson and Scott,[87] Equation [48], predicts a correlation between the half-wave potentials of two series of Schiff bases if the amine fragment is constant in the two

series and the aldehyde fragment varies. This was designated the a/b relationship:

$$\partial E_{\frac{1}{2}}(a)/\partial E_{\frac{1}{2}}(b) = \text{constant} \qquad [49]$$

However, if the aldehyde fragment is kept constant and the amine fragment varied (the c/d relationship), the following equation was shown to apply:

$$\partial E_{\frac{1}{2}}(C)/\partial E_{\frac{1}{2}}(D) = (b_{os}h_N - a^c_{or}k_{CN})/(b_{os}h_N - a^d_{or}k_{CN}) \qquad [50]$$

where a^c_{or} and a^d_{or} are the n.b.m.o. coefficients of the fixed (amine) fragments of the Schiff bases. Equation [50] takes the form of Equation [49] only if $a^c_{or} = a^d_{or}$.

Correlations were drawn between the seven series of Schiff bases (Figs. 5.33 - 5.47) and the slopes calculated by least squares. The data is summarised in Table XXIV. One of the graphs, namely Series A against Series C (Fig. 5.34), is a c/d relationship; the others are all a/b relationships. Excellent correlations were obtained in every case, including that of the c/d relationship which behaves as predicted by the earlier Hückel treatment (Equation [47]) rather than by Equation [50], which indicates that the plot should be curved.

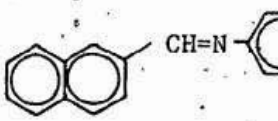
In the above correlations, if Series B is adopted as the standard series, the slopes of the lines obtained by plotting the half-wave potentials of say Series (D) Schiff bases, $E^X_{\frac{1}{2}}(D)$ (x= substituent) against the corresponding half-wave potentials of Series B, $E^X_{\frac{1}{2}}(B)$, provide σ_{Ar} constants (Ar = ) which are

Table XXIV Data from the Correlations of Half-wave Potentials between Series of Schiff bases

Schiff Base Series Correlated	Slope	Relationship
A against B	0.833 ± .025	a/b
A C	0.905 ± .026	c/d
A D	0.692 ± .019	a/b
A E	0.606 ± .027	a/b
A F	0.353 ± .024	a/b
B C	0.933 ± .023	a/b
B D	0.823 ± .020	a/b
B E	0.740 ± .042	a/b
B F	0.373 ± .028	a/b
C D	0.875 ± .019	a/b
C E	0.714 ± .025	a/b
C F	0.395 ± .022	a/b
D E	0.883 ± .022	a/b
D F	0.483 ± .024	a/b
E F	0.547 ± .030	a/b

Table XXV Values of σ_{Ar}

Series A	1.200
Series B	1.000
Series C	0.933
Series D	0.823
Series E	0.740
Series F	0.373

measures of the effect of the change in the structure in the conjugated system of the molecule. These constants are recorded in Table XXV. They are similar in concept to the σ_r proposed by Scott and Jura.[84]

The correlations of Series A with B and Series C with D permit a comparison to be made between the transmission of the effects of a substituent to the reducible > C = N- bond through the carbon and nitrogen atoms respectively. Corresponding Schiff bases in Series A and B, and in Series C and D differ only in the orientation of the > C = N- bond. In Series A and C the substituted benzene ring is attached to the carbon atom (Ar-N = CH-C_6H_4X) while in Series B and D the substituted benzene ring is attached to the nitrogen atom (Ar-CH - N-C_6H_4X).

In Series A and C the substituent effect is transmitted through carbon while in Series B and D it is transmitted through nitrogen. The slopes of the correlations between A and B (0.833 ± .025) and between C and D (0.875 ± .019) indicate that transmission of the substituent effect through carbon is the more efficient. It is also interesting to note that the slopes are approximately of the same magnitude for each pair.

This observation may be qualitatively accounted for in terms of the structure of the Schiff base molecules. The twisting of the molecule about the N-Ar bond reduces the effect of substituents when they occur in the Ar ring. This is to be expected as a consequence of the reduced overlap between the π-system of the substituted benzene ring and that of the rest of the molecule. The similarity of the slopes obtained for the Series A - Series B and Series C - Series D correlations suggests a similarity in the dihedral angles in the two molecules.

5.4 Conclusion

In most linear free energy relationships reported, the Hammett equation has been applied to reaction series in which the range of reactivity between the para- methoxy and para- nitro derivatives, measured in terms of rate or equilibrium constants, is usually less than 5 log units. In the present study the Hammett equation has been successfully applied to reaction series in which the differences in reactivity are much greater. Series of compounds with half-wave potentials varying by as much as 1.1 volts have been successfully correlated. This corresponds to a range of equilibrium constants of approximately 19 log units. This may also be expressed in terms of the magnitudes of the reaction constants, ρ_{SB}. The slope of the correlation between ρ_{SB} (x axis) and ρ_H (Fig. 5.31) is given by the equation:

$$\rho_H = 0.299\ \rho_{SB} + C \qquad [51]$$

where ρ_H and ρ_{SB} are the reaction constants obtained from plots of the half-wave potentials of the compounds in Series A to F against Hammett σ values and σ_{SB} values respectively.

In Equation [51], ρ_H is in log K units while ρ_{SB} is in volts. By converting volts into log K units (1 volt = 16.9 log K units) the slope of the correlation is given by 0.299/16.9 = 0.018. The equation correlating ρ_H and ρ_{SB}, adjusted so that the units are the same on both axes, thus becomes:

$$\rho_H = 0.018\ \rho_{SB} + C.$$

$$\text{i.e.}\quad \rho_{SB} = 55.56\ \rho_H + C'. \qquad [52]$$

The reaction constant for each series of Schiff bases, expressed in log K units, are listed below:

Series	ρ_{SB} (volts)	ρ_{SB} (log K units)
A	.418	23.23
B	.355	19.28
C	.364	20.22
D	.307	17.06
E	.263	14.62
F	.181	10.06

The very large ρ values (log K units) obtained, especially in Series A to D, are approximately of the same absolute magnitude as the reaction (ρ) constant estimated for the gas phase ionisation of the benzyl halides ($\rho^+ \simeq -20$).[88,89] The similarity in the absolute ρ values obtained in this thesis with Thornton's value suggests that solvation effects are virtually absent in the formation of radical anions under the conditions in which the half-wave potentials were measured. Thus, in the thermodynamic cycle discussed in Chapter 3.1 the free energy of addition of an electron to the neutral molecule in dimethylformamide, ΔG_S, is approximately equal to the electron affinity of the molecule in the gas phase, E_f. This observation more than justifies the assumption made by Scott and Jura[54] and also the assumption in this thesis that solvent effects on the reduction potentials of Schiff bases are independent of the structure of the Schiff bases, since solvent effects appear to be both relatively and absolutely unimportant.

The above conclusions are in agreement with conclusions based

on other data summarised by Ritchie in his review of interactions in dipolar aprotic solvents,[90] namely that:

(a) Substituent effects on the acidities of phenols are reported to be much greater in dimethylformamide than in methanol. In methanol, the smaller effect is attributed to "the change in the hydrogen-bonding stabilisation of the phenoxide simultaneously caused by the substituent." This compensating factor is absent in dimethylformamide and substituent effects are, therefore, larger. Hence, solvent effects can modify the influence of substituents.

(b) The reaction of azide ions with several substrates and of methyl halides with nucleophiles are faster in dimethylformamide than in methanol by a factor of 10^2 to 10^6. It is suggested that the work required to break down the initial solvation shell is an important part of the activation energy for reactions in methanol. Such effects are thought to be minimal in dimethylformamide and this factor is assumed to account for part of the increase in the reaction rates mentioned above.

Further studies of substituent and other structural effects in dimethylformamide might be of considerable interest, since the data obtained would appear to be essentially free of complications due to solvent-solute interactions and the much larger substituent effects obtained insures that the effects of smaller structural variations can be observed more accurately. Finally, Dewar[91] has stated that it is not possible to develop quantitative theories of reactivity based only on

meta- and para- substituted benzene derivatives (for which copious data are available). It is necessary to investigate substituent effects in other systems which also lend themselves to theoretical calculations. The Schiff bases examined in this study satisfy both criteria. The data may therefore be particularly useful in future theoretical investigations of substituent effects and may contribute to a better understanding of the factors involved.

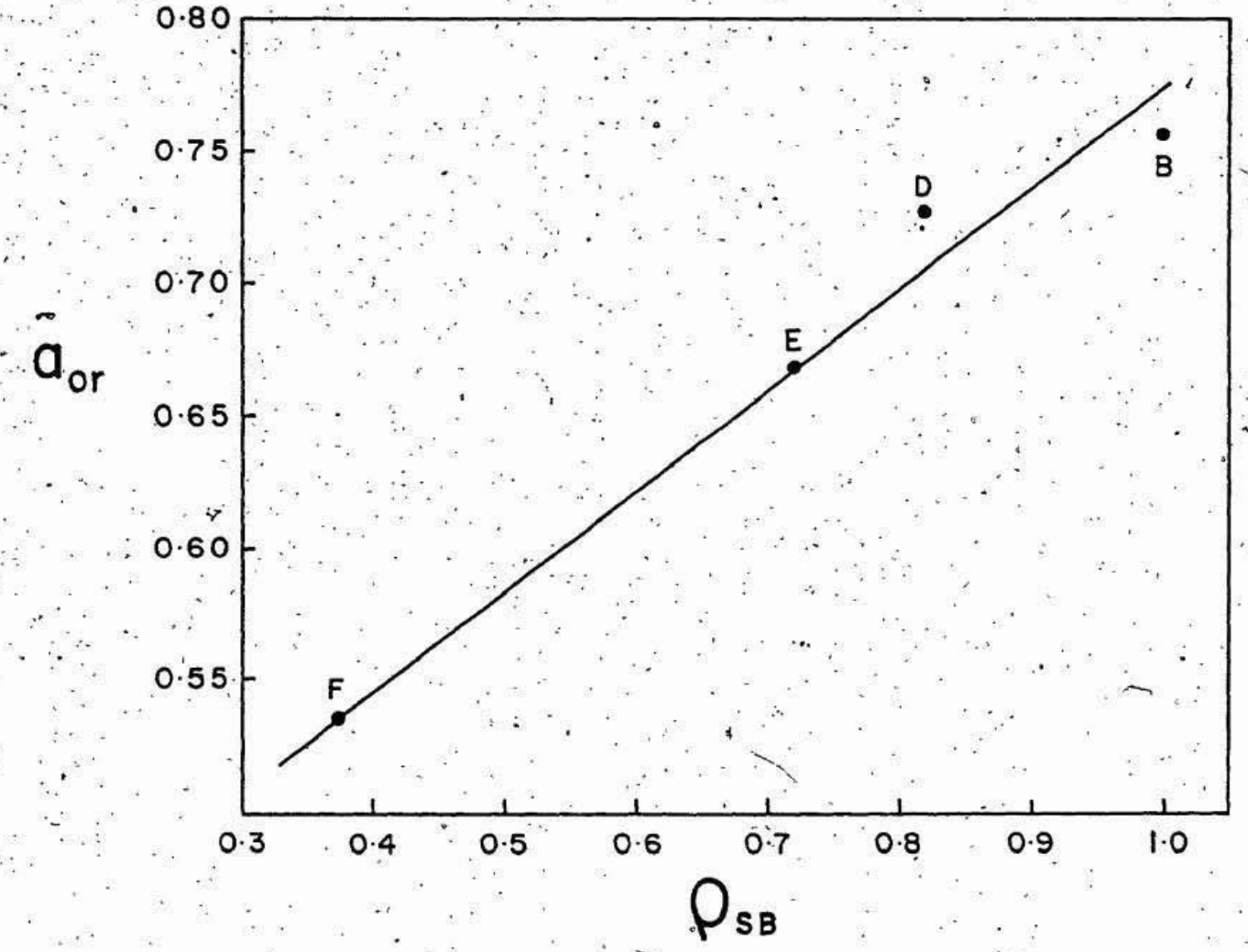


Fig. 5.32 Correlation of n.b.m.o. coefficients, a_{or}, for Series B, D, E and F Schiff bases with ρ_{SB}.

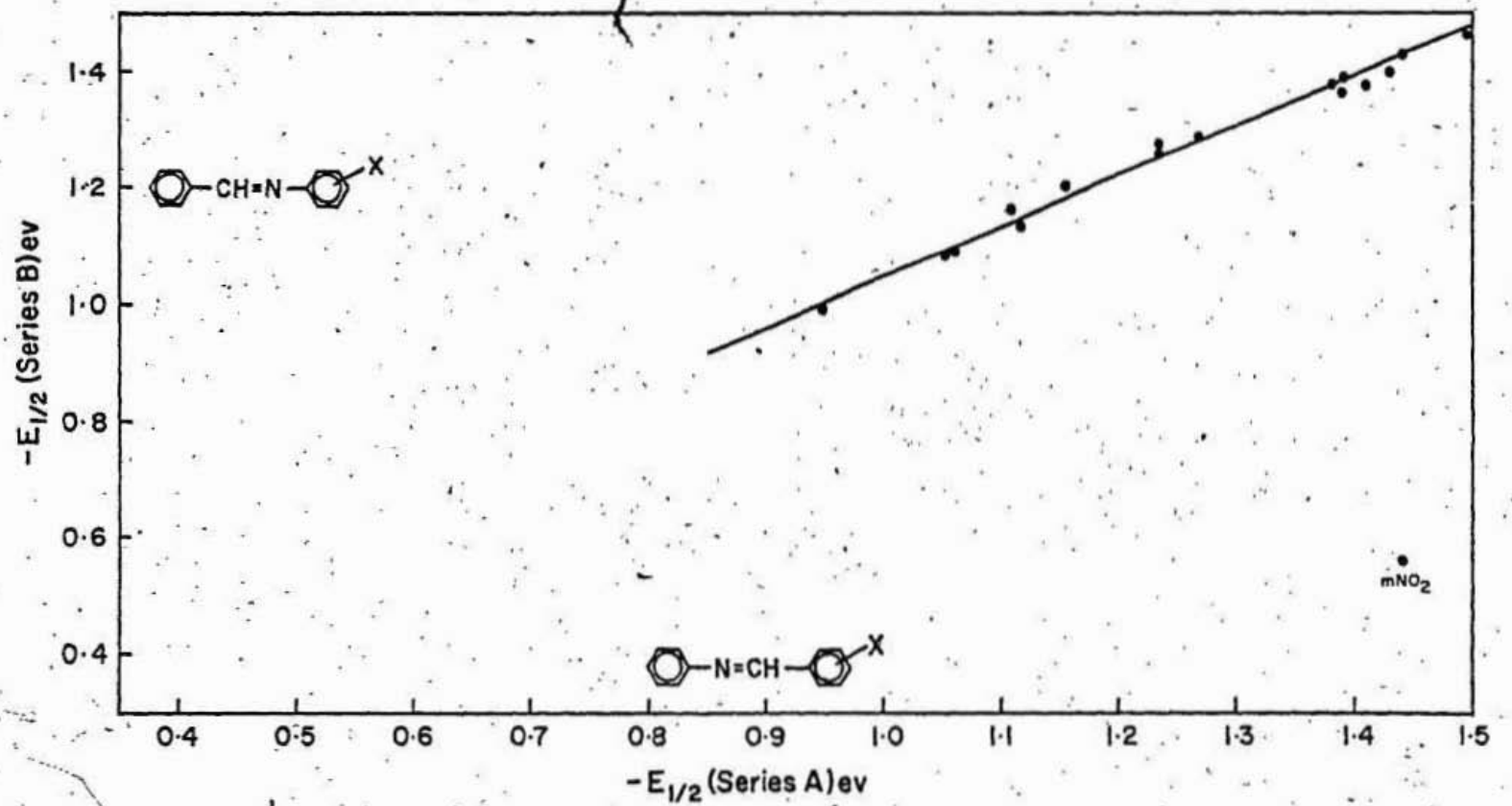


Fig. 5.33 Correlation of half-wave potentials of compounds in Series A with those of corresponding compounds in Series B.

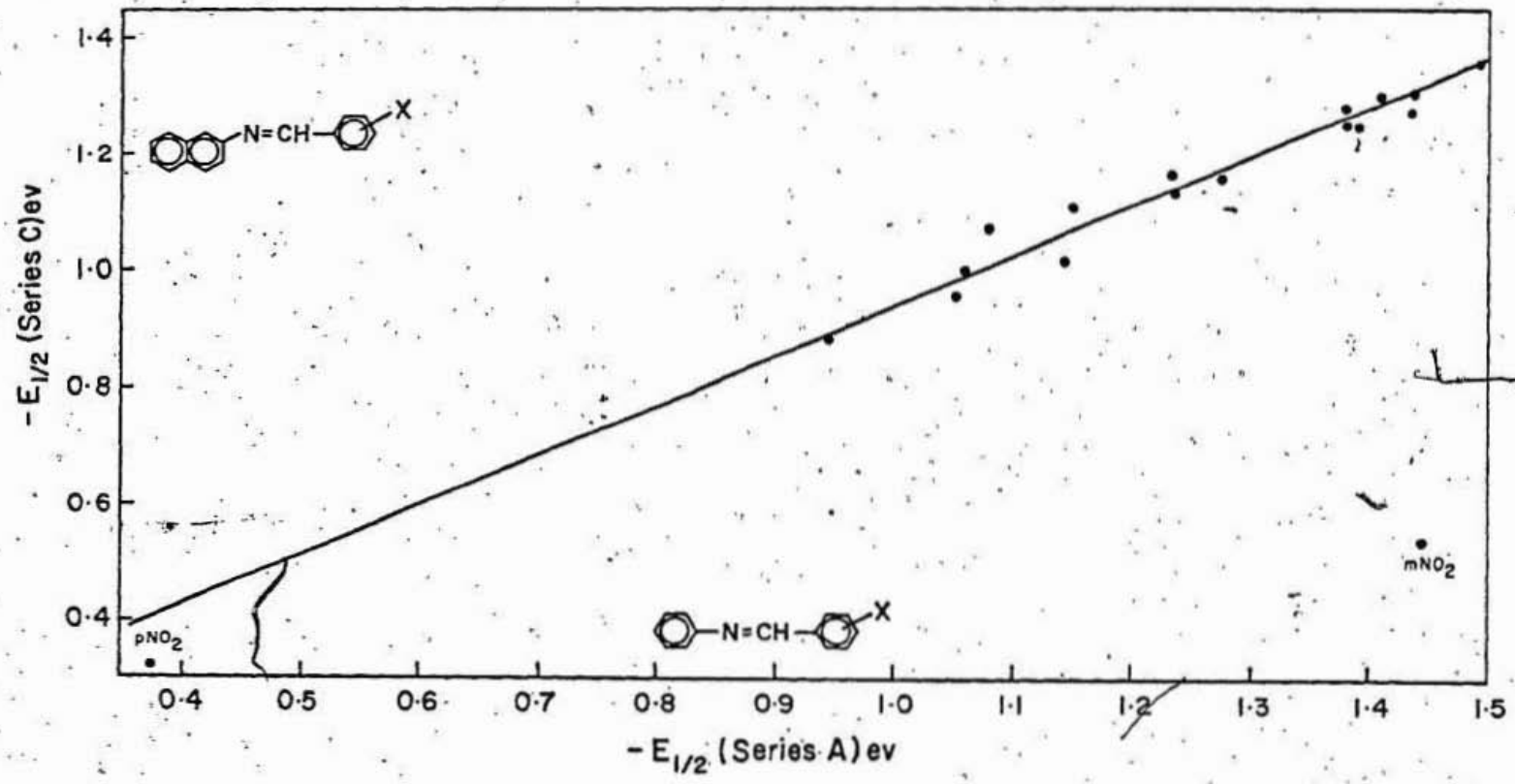


Fig. 5.34 Correlation of half-wave potentials of compounds in Series A with those of corresponding compounds in Series C.

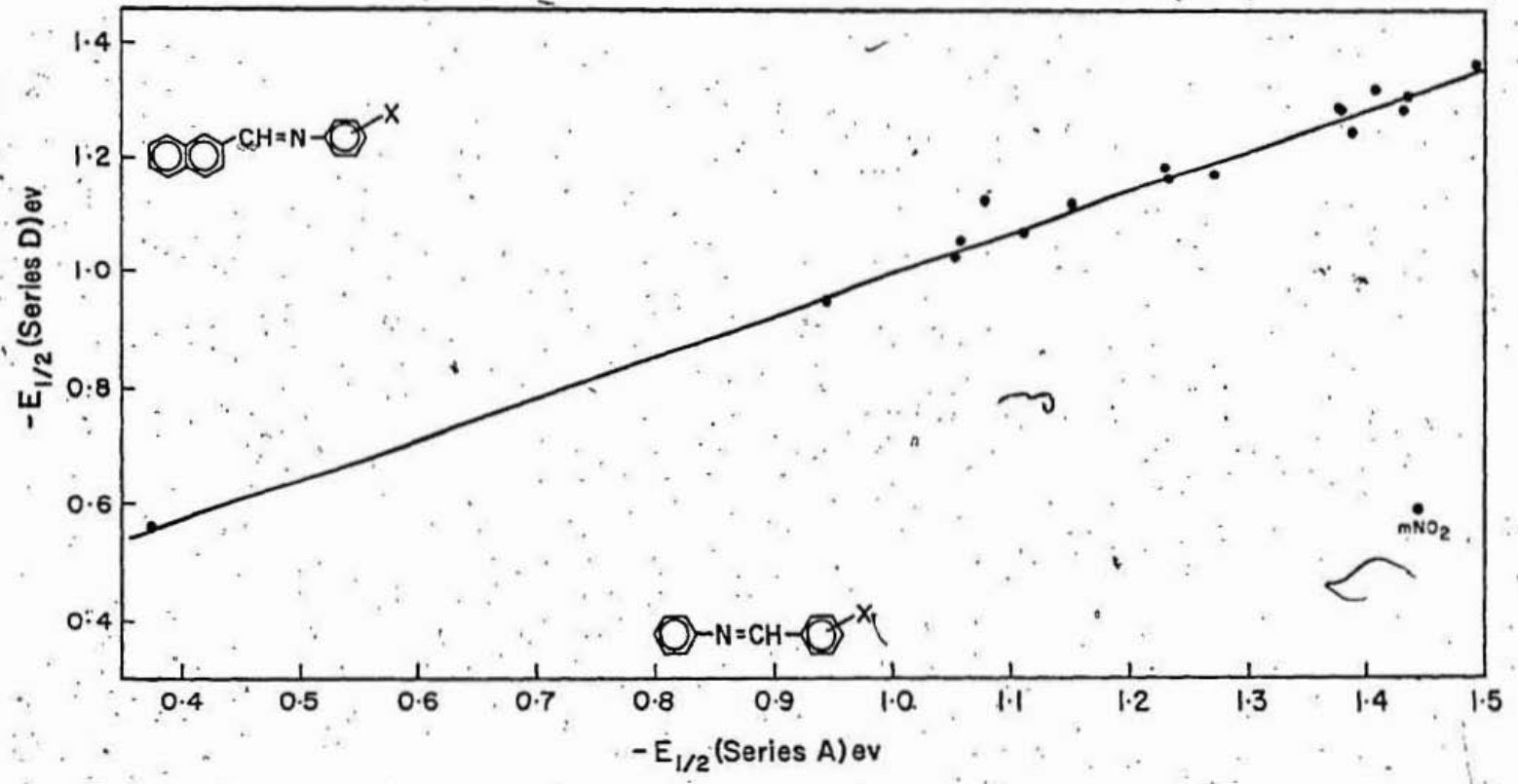


Fig. 5.35 Corrélation of half-wave potentials of compounds in Series A with those of corresponding compounds in Series D.

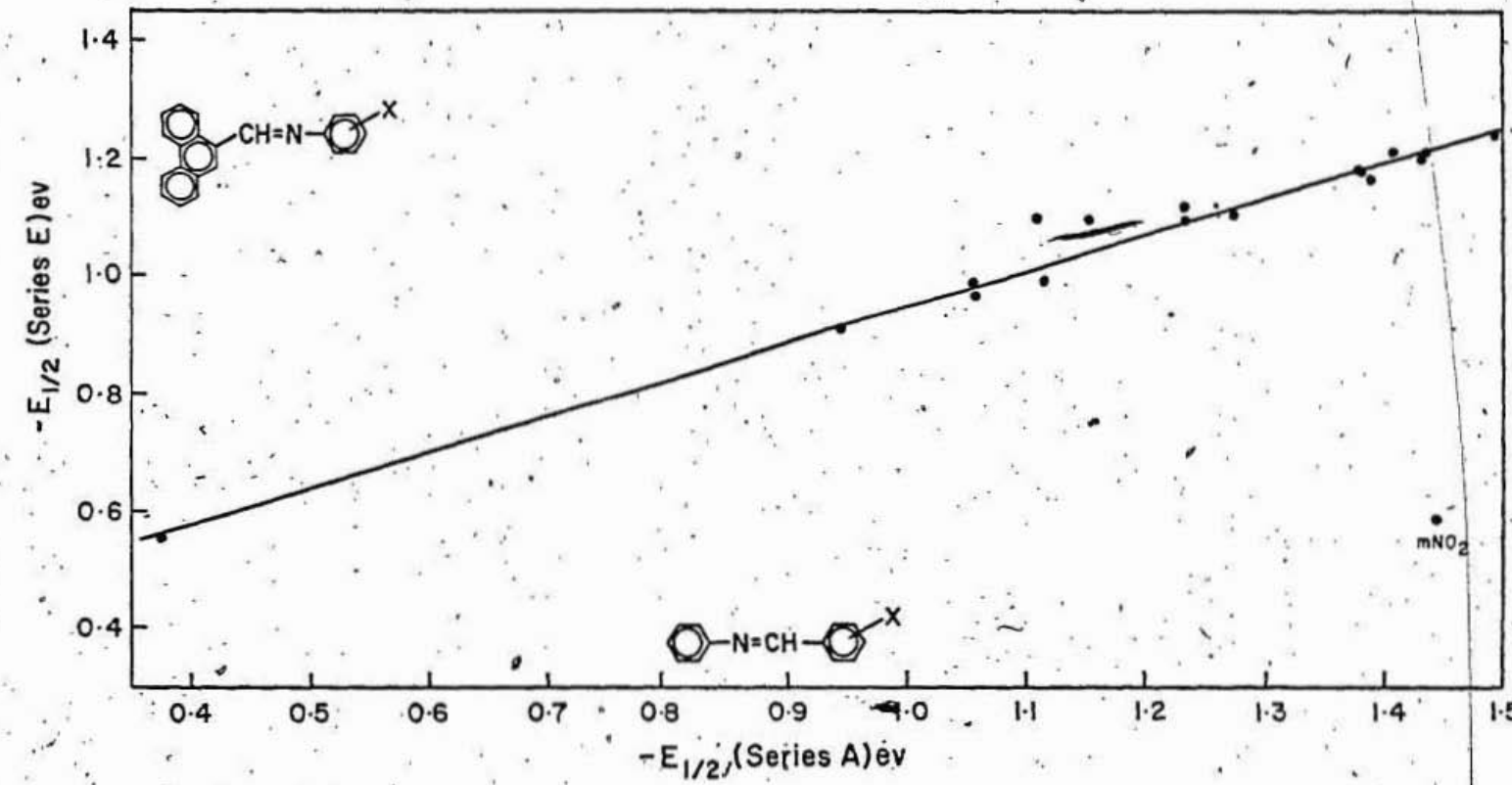


Fig. 5.36 Correlation of half-wave potentials of compounds in Series A with those of corresponding compounds in Series E.

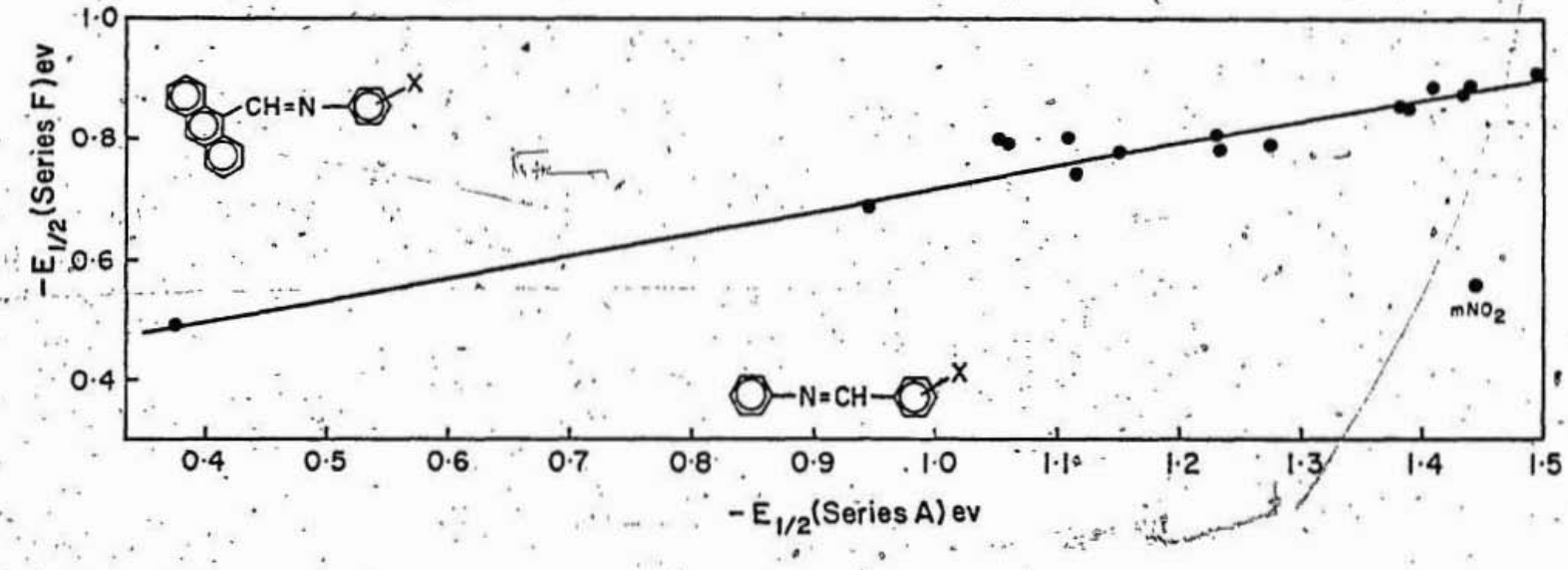


Fig. 5.37 Correlation of half-wave potentials of compounds in Series A with those of corresponding compounds in Series F.

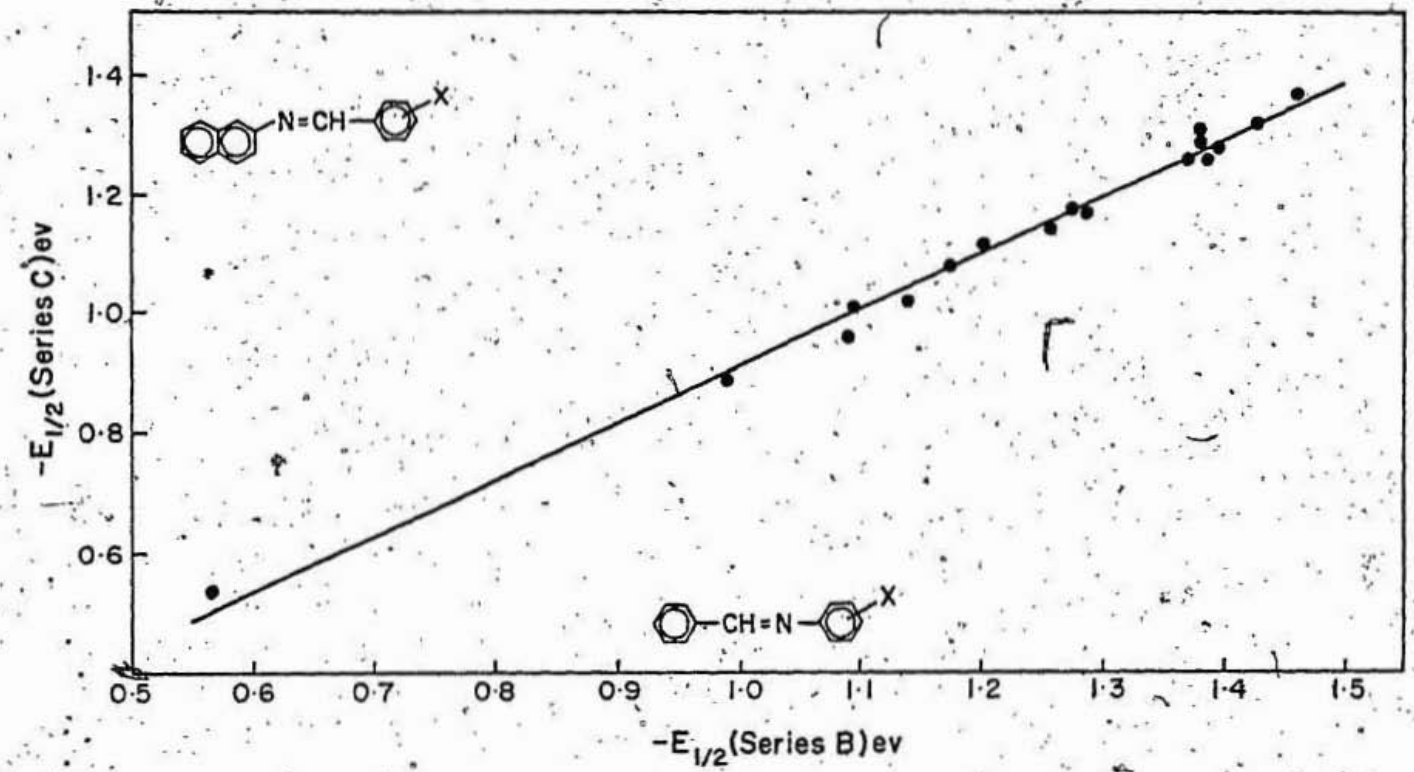


Fig. 5.38 Correlation of half-wave potentials of compounds in Series B with those of corresponding compounds in Series C.

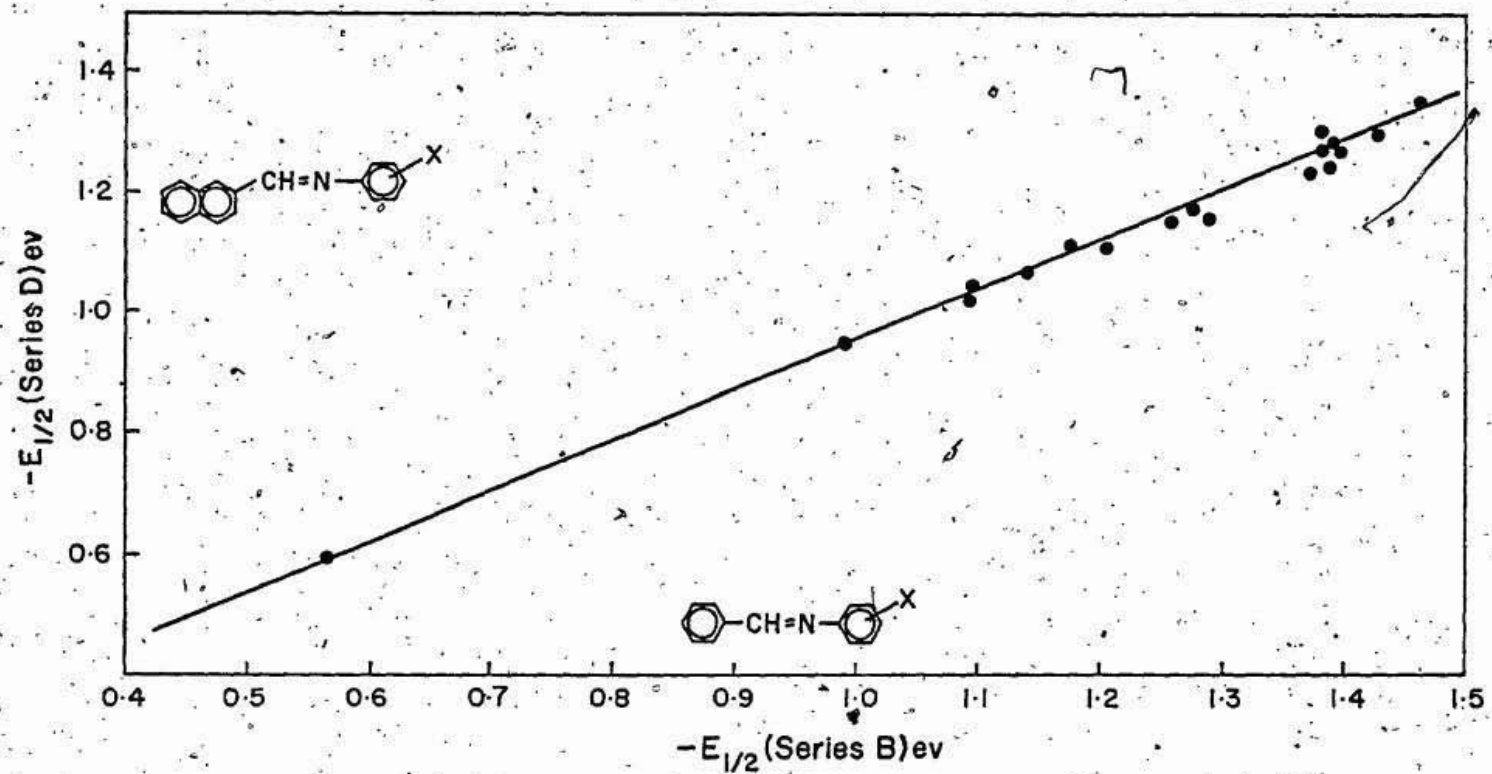


Fig. 5.39 Correlation of half-wave potentials of compounds in Series B with those of corresponding compounds in Series D.

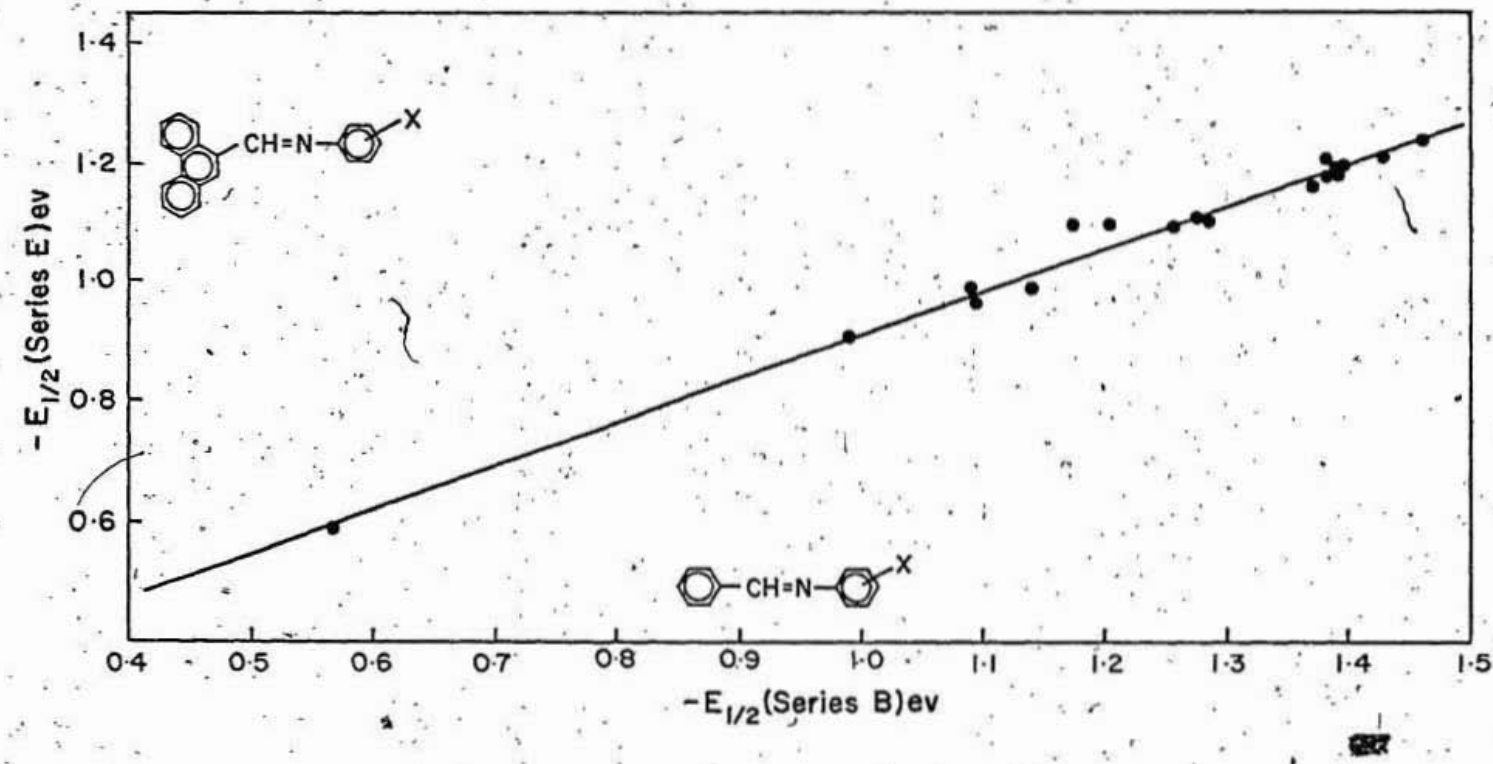


Fig. 5.40 Correlation of half-wave potentials of compounds in Series B with those of corresponding compounds in Series E.

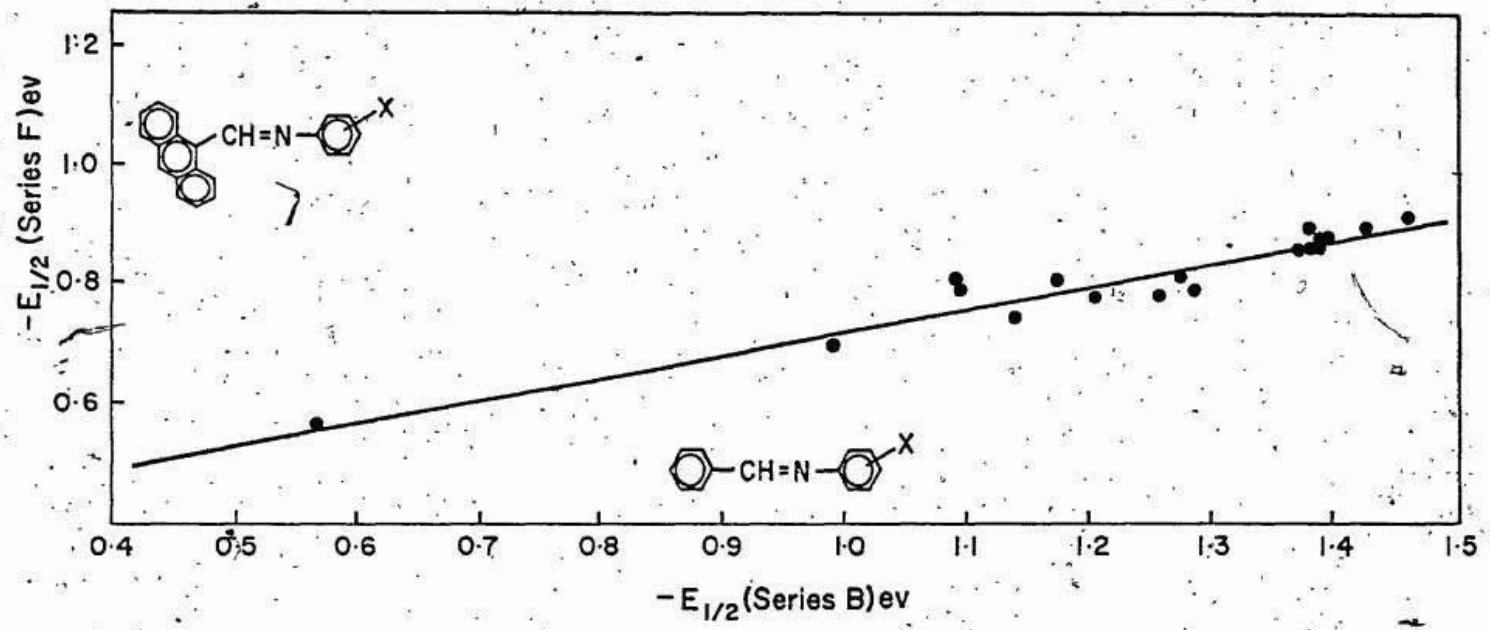


Fig. 5.41 Correlation of half-wave potentials of compounds in Series B with those of corresponding compounds in Series F.

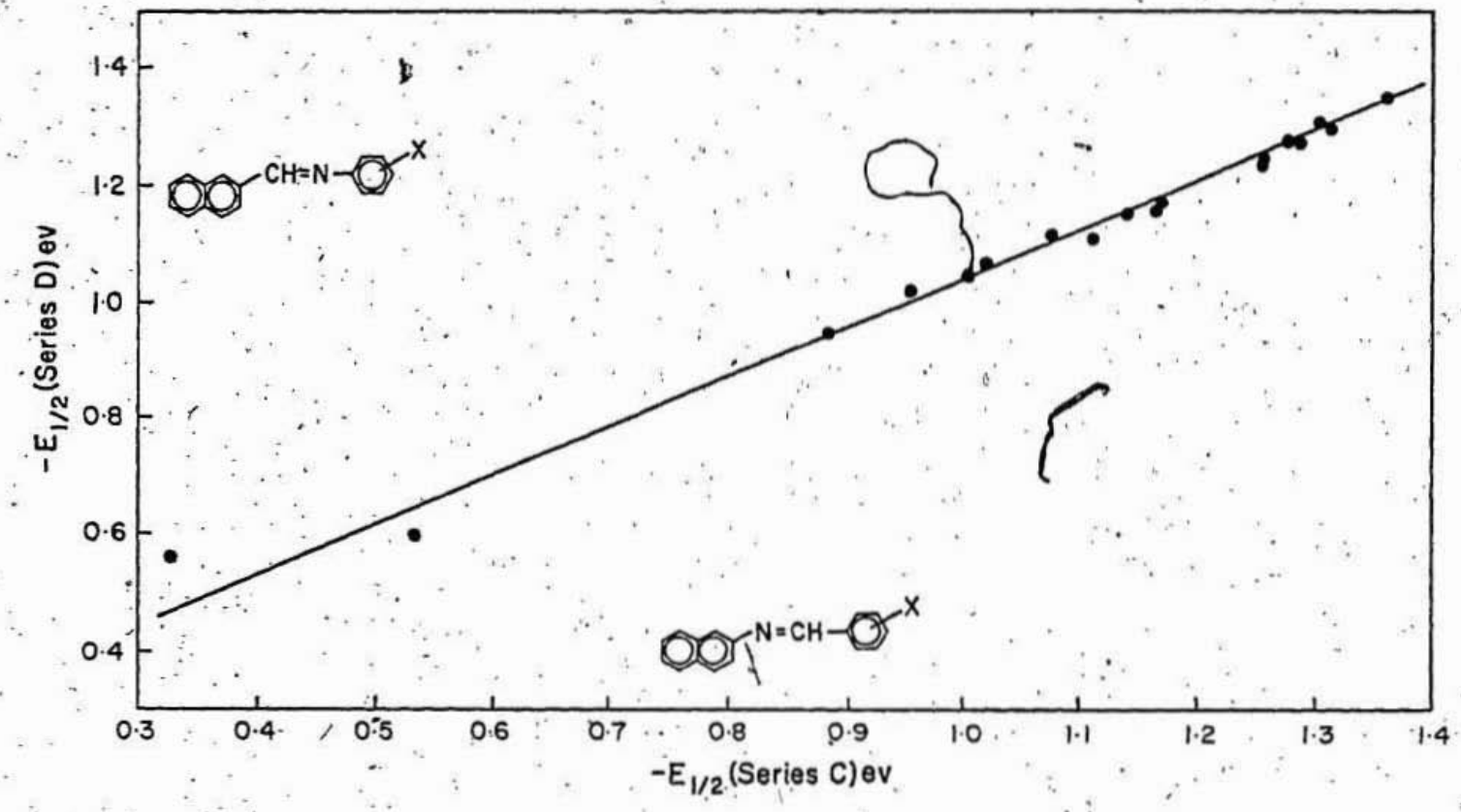


Fig. 5.42 Correlation of half-wave potentials of compounds in Series C with those of corresponding compounds in Series D.

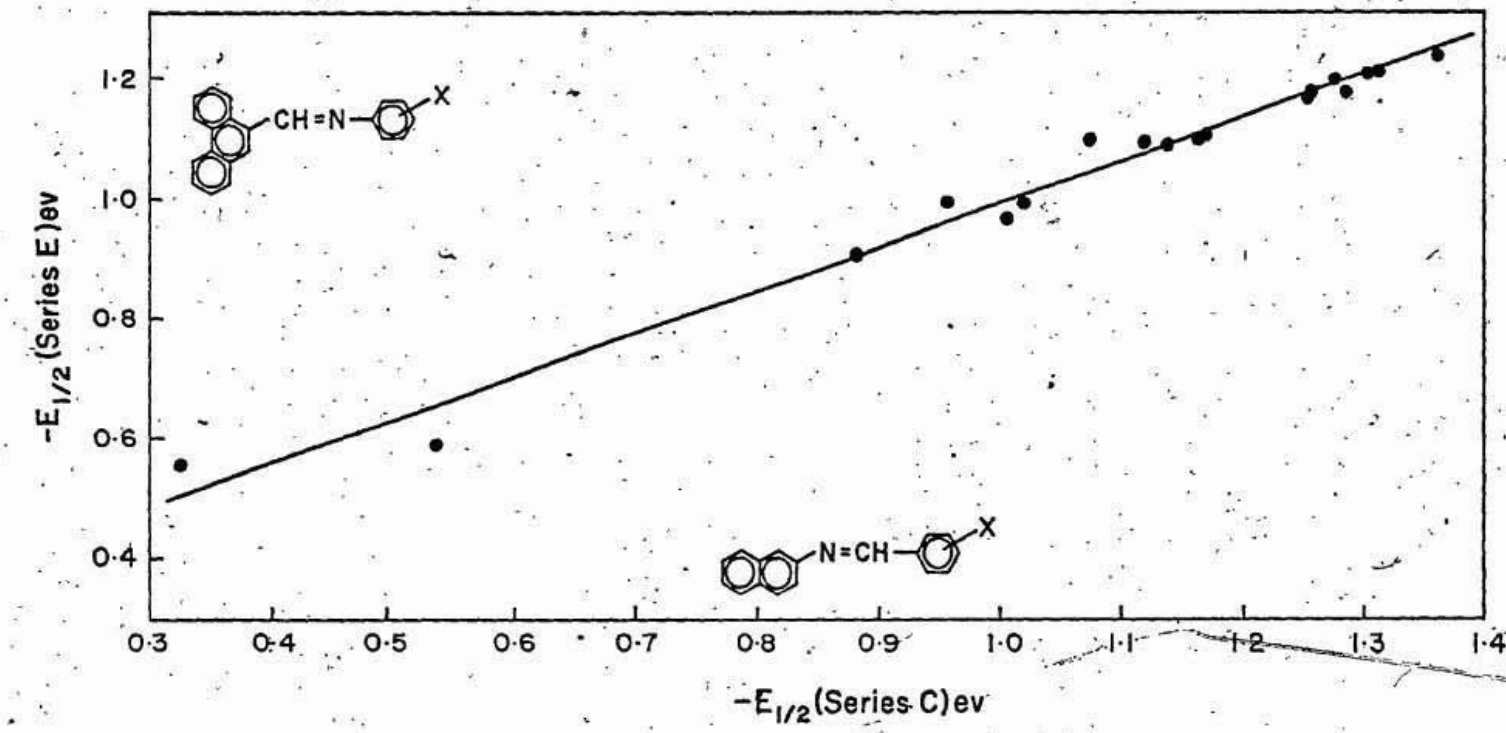


Fig. 5.43 Correlation of half-wave potentials of compounds in Series C with those of corresponding compounds in Series E.

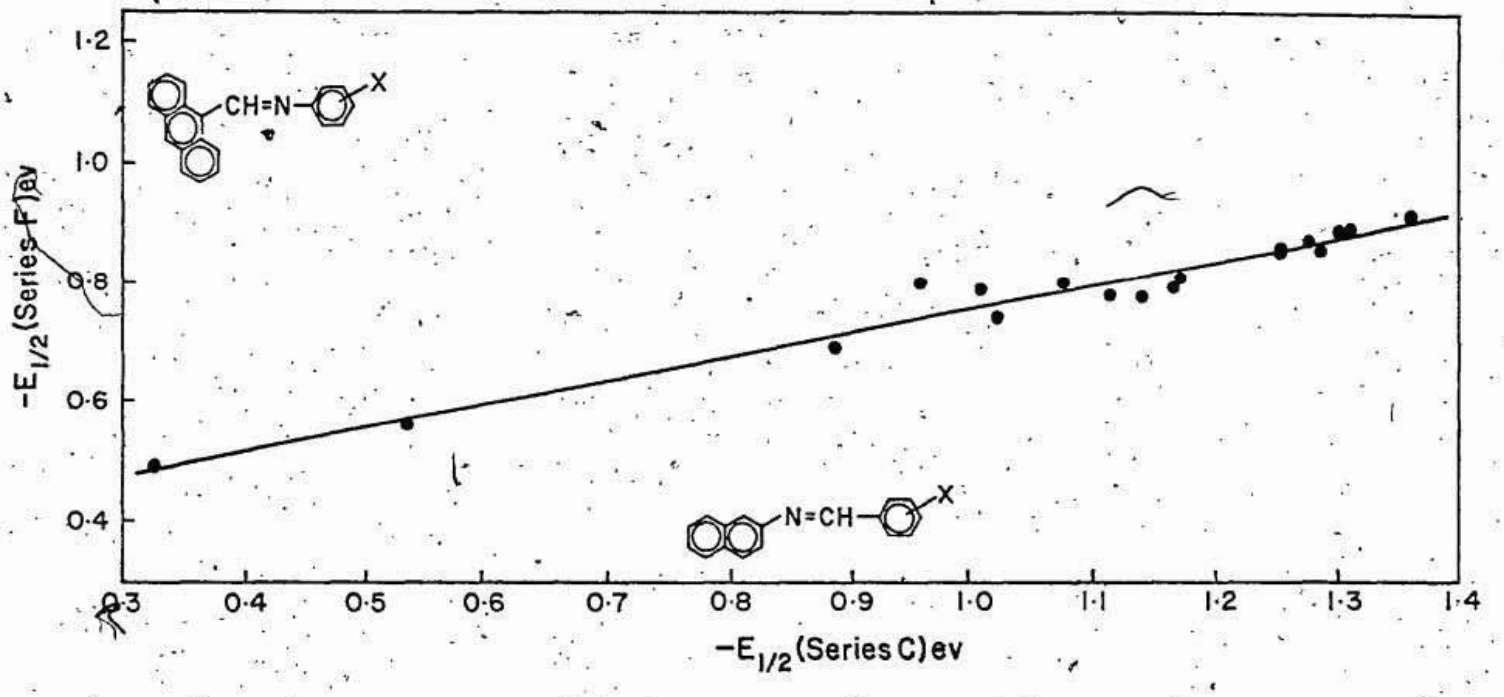


Fig. 5.44 Correlation of half-wave potentials of compounds in Series C with those of corresponding compounds in Series F.

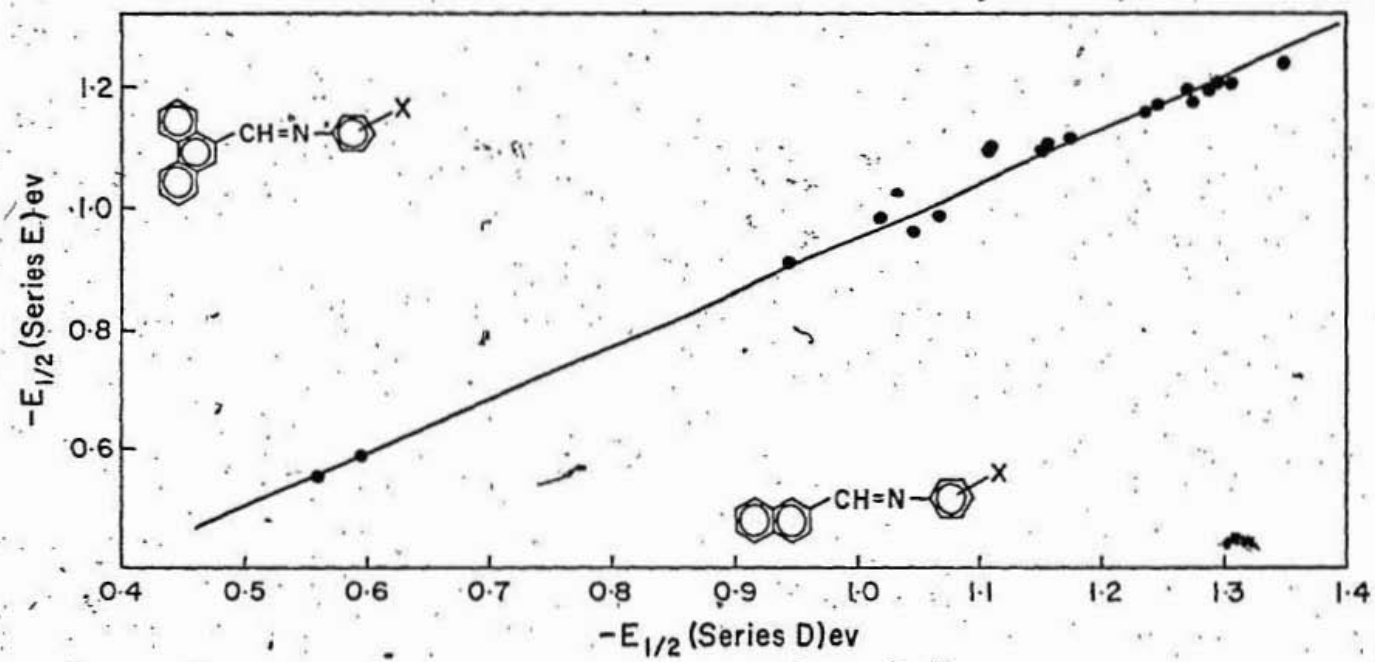


Fig. 5.45 Correlation of half-wave potentials of compounds in Series D with those of corresponding compounds in Series E.

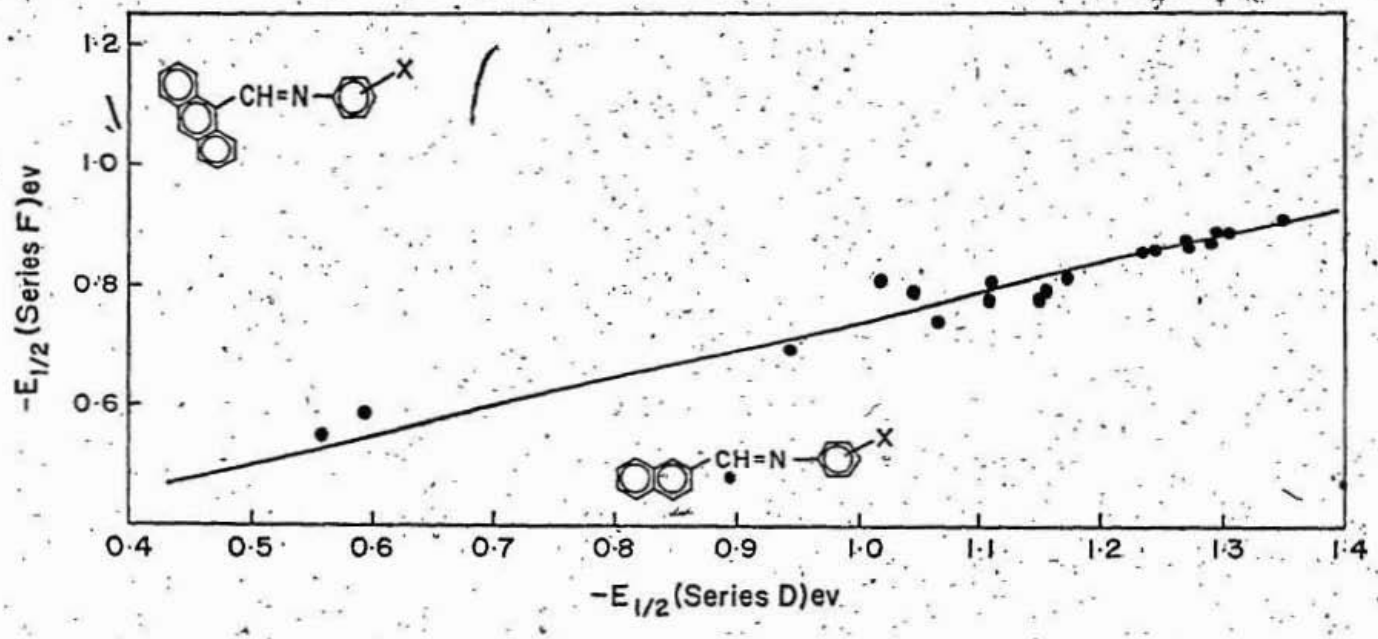


Fig. 5.46 Correlation of half-wave potentials of compounds in Series D with those of corresponding compounds in Series F.

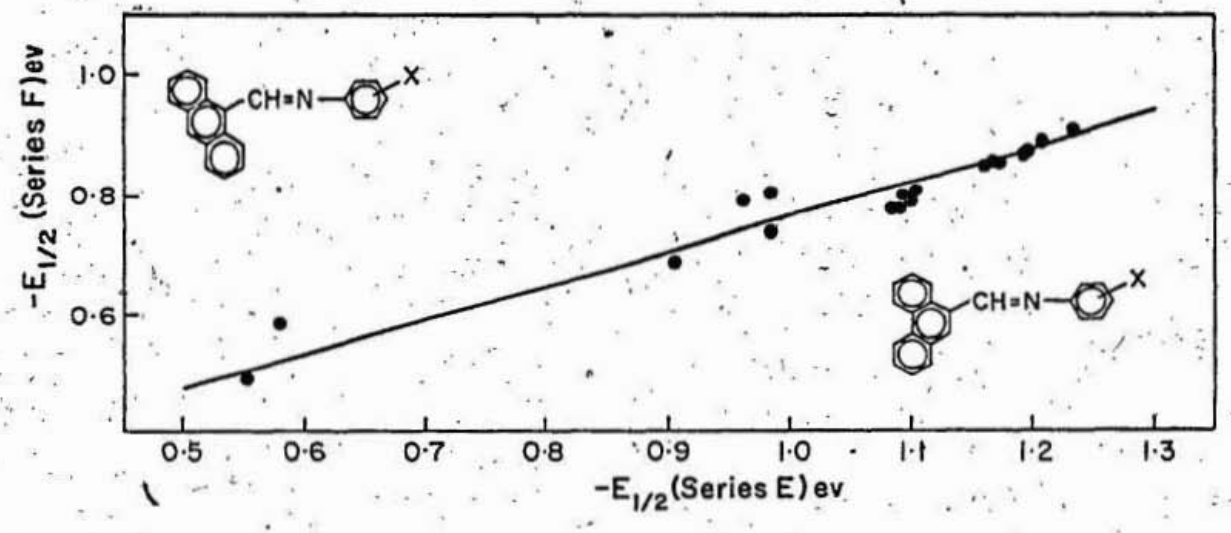


Fig. 5.47 Correlation of half-wave potentials of compounds in Series E with those of corresponding compounds in Series F.

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